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Impact of Natural Hydrocarbons on Air Quality

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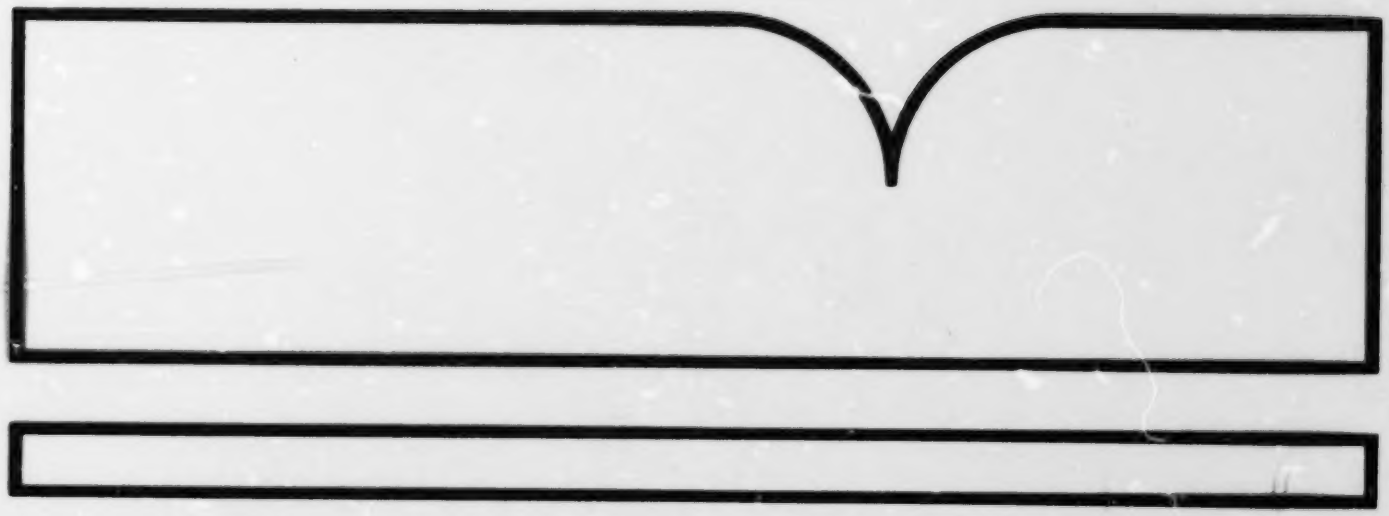

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Impact of Natural Hydrocarbons on Air Quality

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IMPACT OF NATURAL HYDROCARBONS ON AIR QUALITY

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ABSTRACT

The emissions, reactivities, and ozone-forming potential of natural hydrocarbons are discussed. A review of the data available on emission levels for natural hydrocarbons indicates that much more information is needed in order to quantify the absolute emission levels, because emissions data do not agree with ambient air measurements. These ambient air measurements suggest that the previously-published value of 9×10^8 ton/yr needs to be lowered to 10^6-10^7 ton/yr. Emissions may be overpredicted by a factor of 15 to 20, as indicated by back calculations using a simple diffusion trajectory model.

Isoprene, when compared to the monoterpenes, is much more efficient in producing ozone through photooxidation in the presence of NO_x. This greater ozone production apparently occurs because of the large amount of carbon consumed in the formation of aerosols for the monoterpenes. Since rural areas have very low levels of NO_x, vegetative emissions may in fact act as sinks for ozone rather than as sources. All areas investigated show very low levels of natural hydrocarbons, suggesting that even if NO_x were available, very low levels of ozone would be produced. Air quality is thus not found to be significantly affected by vegetative emissions.

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I'm also indebted to Northrop Services for the use of their data on the smog chamber studies of natural hydrocarbon and to Ms. A. McElroy for typing the many iterations of this document.

SECTION 1

INTRODUCTION

The involvement of hydrocarbons (HC's) in the formation of photochemical smog is well documented (1-4). Also generally accepted is that both the type and the amount of HC are important in the formation of photochemical smog. If ozone is taken as the indicator for smog formation, at a favorable hydrocarbon to NO_x ratio (HC/NO_x) olefins are found to produce ozone most quickly, followed by the substituted aromatics and then the slow-reacting paraffins. However, if reduced visibility (or aerosols) is taken as the photochemical smog indicator, then the substituted aromatics and the olefins of higher molecular weight (C_6^+) are the largest contributors.

Natural HC's, i.e., isoprene and the monoterpenes, are olefinic compounds that are expected to produce both ozone and aerosol. The question then arises, can natural HC's be a significant source of ozone and visibility reduction in rural areas? Also, does vegetation contribute to photochemical air pollution problems that exist in most large metropolitan regions?

In this paper we would like to critically review the relevant literature concerning natural HC's and their role in pollution problems observed in urban and rural areas. The HC's to be considered are the monoterpenes ($C_{10}H_{16}$) and isoprene (C_5H_8). Other natural HC's, such as methane (CH_4) and stress-evolved ethene (C_2H_4), will not be considered, since CH_4 is thought to be unreactive and C_2H_4 emissions are too small to be significant (5-7). The specific topics covered are: (1) HC emissions, (2) reactivities of natural HC's, (3) product formation, and (4) source-receptor relationships.

SECTION 2

CONCLUSIONS

Although additional information is needed in order to firmly establish the role of natural HC's in ozone formation, the present data suggest emissions from vegetation are not likely to have significant effects on air quality. All gas-phase HC analyses and carbon aerosol studies suggest that natural HC's do not exist at sufficiently high concentrations to affect air quality in either urban or rural areas. Emissions data do not agree with ambient air measurements. Those measurements suggest that the previously published value of 9×10^8 ton/yr needs to be lowered to 10^6-10^7 ton/yr.

Isoprene and the monoterpenes produce ozone when photooxidized in the presence of NO_x. However, they are not efficient ozone producers since a large amount of carbon is consumed in the production of aerosols. Because of the aerosol production, the natural HC's may contribute to visibility reduction in pristine areas.

SECTION 3

RECOMMENDATIONS

Additional work in the area of vegetative HC emissions should include:

(1) Establishment of better emission values. In-situ vertical profile measurements are recommended over enclosure techniques. The enclosure and simulated environmental chamber techniques suffer from possible pertubation of the normal environment, which results in unusual emissions. Also, greater understanding and better measurement of the biomass factor is needed in the enclosure techniques.

(2) Better collection and analyses of gases and aerosols in rural and urban areas are needed. These improvements should include a measure of the C^{14}/C^{12} ratio for the organics, especially for the fine particulate fraction. The C^{14}/C^{12} ratio in living matter is not the same as that found in petroleum and coal (8, 9), so one can measure the natural versus fossil carbon contribution to the atmosphere by determining this ratio.

(3) Additional smog chamber studies are needed in order to determine the ultimate fate of the photooxidation products of natural HC's. Previous studies in this area have met with only limited success and have only sketchily defined the mechanism for terpene photooxidation. Until all products are identified, the mechanism will remain this way.

(4) Modeling exercises are needed in order to establish the importance of natural HC's to urban and rural air quality. Various emission scenerios could establish the importance of natural versus anthropogenic emissions. These computations would then be compared to observed air quality data in order to assess the emission scenerio most compatible with air quality data.

(5) Finally, we must understand why uninhabited areas (e.g., the Smoky Mountains) have reduced visibility. The data in the area show little or no carbon in the fine-particulate fraction but yet reduced visibility occurs, and was apparently occurring long before the industrialization of America. Understanding reduced visibility in the mountain areas is necessary if we are to understand the role of natural HC's to air quality.

SECTION 4

HC EMISSIONS

Total emission calculations of terpenoid HC's were first made by Went (10). The actual computation of this often-cited work is based on data supplied by A.J. Haagen-Smit (through a private communication with Dr. Went). Haagen-Smit analyzed air that was passed over shrubs of Artemisia tridentata (Basin sagebrush). After combustion and transformation of the HC to CO_2, Haagen-Smith calculated that approximately 50 kg $day^{-1}km^{-2}$ of emissions resulted. From this work, Went extrapolated that 1.75×10^8 ton/yr of volatile natural HC is liberated worldwide.

The numerous assumptions in Went's calculation include that: the average number of emission days is 100 per/year; the vegetation covers 2×10^5 km^2 in the western United States; coniferous and hardwood forest produce approximately the same amount of volatile organic matter; and, the earth's total vegetative area is 10^7 km^2. Obviously, Went's number rests upon few measured parameters. Also, the basis of all Went's calculations, the Haagen-Smith work, is not given in detail, which makes validation of the initial number difficult. For example, if the air Haagen-Smith used to fumigate the vegetation contained significant background HC, then the estimated emissions level from the number is grossly in error, since the change in CO_2 would be small upon combustion. If the change in CO_2 were not used in the calculation, then the emission would be too large.

More systematic research of HC emissions was performed by Rasmussen and Went (11), who studied several locations in the United States and one in Holland. Ambient air samples, as well as plants with plastic containers, covered were analyzed. The HC's identified by retention times on the gas chromatograph (GC) include; isoprene, α-and β-pinene, limonene, and myrcene. Additional hydrocarbons, Δ^3-carene, myrcene and p-cymene, were

tested for retention times, but Rasmussen and Went were not explicit in stating if those HC's were detected in the ambient air. The direct measurements of volatile organics in the atmosphere (presumably the summation of the terpenes and isoprene) showed an average concentration of 10 ppb (presumably V/V). This value was then assumed to exist in a 2-km column of air, with a yearly production rate of 270 days. Using an estimated, vegetated land area of $10^{18} cm^2$, the total world production was calculated to be 4.38×10^8 ton/yr. The investigators also calculated $20\text{-}40 \times 10^7$ ton/yr by the enclosed plastic container technique, which makes the two above methods agree within a factor of roughly two, and suggests that the earlier estimate of Went is too low.

The work of Arnts et al. (12) that will be described later does not substantiate the 2-km column height containing 10 ppb terpene. In fact, the terpene concentration was found to decrease exponentially with height. At 10 m above a tree canopy, the terpene concentration was determined as less than 30% of that found just at the canopy height. Considering these factors, the calculations made by Rasmussen and Went would be reduced by a factor of over 2000. Thus, the 4.38×10^8 ton/yr would be reduced to 2.2×10^5 ton/yr.

In another study, Ripperton et al. (13,14) found the α- and β-pinene/ozone reactions to be very fast (0.8×10^5 liter $mole^{-1} sec^{-1}$ and 0.25×10^5 liter $mole^{-1} sec^{-1}$). The authors reasoned that ozone may have destroyed a portion of the emitted terpenes and concluded, because of the ozone/terpene reaction, that the original estimates of Rasmussen and Went should be multiplied by a factor of 2 to 10.

Although these calculations by Ripperton et al. are qualitatively correct, the two-to-ten fold increase in terpene concentration is difficult to accept. Since the terpene concentrations were measured within the forest canopy, any effect from ozone should not be large, and the levels of terpene observed should be close to the true concentrations emitted without reaction. If for example, the ozone concentration is approximately 30 ppb in the forested area (15), then the half-life is approximately one day for isoprene and a few hours less for α-pinene. (This calculation assumes a constant

reservoir of ozone from a pseudo first-order reaction, though ozone is actually depleted near the ground by both terpene reaction and dry deposition.) The OH concentration is also assumed to be zero due to minimal sunlight penetration into the canopy. The correction for ozone effects made by Ripperton et. al. is in fact probably no more than a few percent, if 30 ppb of O_3 and 10 ppb of terpene are involved, which falls well within the errors contained in the original calculations of Rasmussen and Went.

Rasmussen (16) in a later study measured several terpenes emitted from various types of deciduous and coniferous vegetation. These HC's were α, and β-pinene, camphene, limonene, myrcene, and β-phellandrene, isoprene was also found to be emitted from hardwoods. Emission rates were measured by placing an undamaged portion of the plant sample in a glass bell jar. The HC buildup in the bell jar was then measured at several levels of radiation exposure (50 to 1200 ftc) and at two different temperatures (17 and 30-32^{o}C). Coniferous types of vegetation were found to emit terpene independently of light, while deciduous plants emitted isoprene in a linear dependence upon light intensity. Alpha-pinene emissions from conifers were found to increase by a factor of 4 to 7.5 when the temperature was increased from 17^{o}C to 30-32^{o}C.

Rasmussen further gives the percentage of hardwood and softwood forest in the United States. From the foliage per acre given by others (17-19), global natural HC emissions are given. Rasmussen estimates from his emission rates that a 10-cm foliar canopy would result in a worldwide natural HC level of 23.4 x 10^6 metric ton/yr. A 50-cm thick canopy would result in 117 x 10^6 metric ton/yr; 75 cm in 185 x 10^6 metric ton/yr; and finally 200 cm in 464 x 10^6 metric ton/yr. The abstract of the paper suggests that the 75-cm canopy value of 175 x 10^6 metric ton/yr is the most reasonable. We have been unable to determine from the manuscript his method of extrapolating from the individual emission rates of the clipped branches to worldwide emissions or the validity of this method.

In successive studies, Tyson et al. (19) and Dement et al. (20) measured emissions from the sagebrush, Salvia mellifera. This shrub is distributed throughout the coastal region of California and covers approximately 45% of the site studied. The investigators found that the emission levels of terpene were over an order of magnitude lower than the findings of Went (10), i.e., 3 kg day^{-1} km^2 versus Went's 50 kg day^{-1} km^{-2}. In the Dement et al. study, the same sagebrush was investigated under light and dark conditions, as well as different relative humidities and temperatures. These investigators found that the emission rates were dependent upon leaf temperature, but were independent of light. They also found that relative humidity was a factor in the emissions. Thus, emissions almost doubled (3.1 $\mu g/dm^2$ versus 5.8 $\mu g/dm^2$) when the air dew point was 22°C compared to 0°C. Also determined was that the level of HC an excised branch will liberate is more than twice that of an uncut branch (13.1 $\mu g/dm^2$ versus 5.8 $\mu g/dm^2$, at D.P. = 22°C). This latter finding is interesting in that it suggests the Rasmussen value obtained on cut branches overestimates HC emissions.

The Research Triangle Institute (RTI) in 1974 (21) measured natural emissions of gaseous organic compounds in the Ohio area. In this report worldwide emissions were also calculated. The authors suggest that the often cited work of Went (10) and Rasmussen and Went (11) have serious shortcomgings in that only terpenes and their derivatives are considered; the RTI report lists a much larger number of organic compounds liberated by vegetation. The natural emissions estimate of RTI is based on the carbon fixation process, assuming that 10% of the available carbon goes to hydrocarbon emissions. By this estimate, Rasmussen's emission estimates are too low by a factor from two to ten. The total emissions calculated by RTI are 0.4-1.2 x 10^{10} ton/yr, with an average of 8 x 10^9 ton/yr.

We have difficulty evaluating RTI's estimate, since it considers all organic compounds including the oxygenates. Also, the original estimate by Went of 1.75 x 10^8 ton/yr was, as stated earlier, based on the Haagen-Smit work, in which air was passed over sagebrush and all the organic compounds were analyzed. Therefore any other organics liberated by the sagebrush would also have been oxidized to yield CO_2. Again, the work of Rasmussen and Went is probably in error since a uniform HC column is assumed.

Furthermore, the 10% emission of the CO_2 fixation suggested by RTI is not verified. As stated in the RTI report, "ten percent was an estimate which appeared to be reasonable." The ten percent may be reasonable, but two points are highly unlikely: (1) that all the material expired by the plants is necessarily volatile, and (2) that all the HC's would necessarily participate in photochemical smog production, i.e. saturated low-molecular-weight HC's.

The most extensive work on the measurement of emission rates has been performed by Zimmerman (22, 23). His measurement technique involves an in-situ enclosure of a portion of the tree or foliage sample with a Teflon bag. The bag is partially emptied and then flushed with metered volumes of air. The organic compounds are collected in canisters and returned to the laboratory for detailed analyses.

In these studies, Zimmerman not only measured emissions from various types of vegetation, but also examined the different plant species in different parts of the United States. The emission rates of some of the plant species, as given by Zimmerman, are shown in Table 1. Table 2 shows the major emissions from selected vegetation. In Figure 1, the structures of selected natural HC's are illustrated. Zimmerman further divides the emission rates into different biotic regions according to Dasmann (24). He sub divides these regions into latitudinal sectors for average sunlight and temperature. Drawn from these assumptions, Table 3 summarizes regional and total global emissions. The total worldwide emissions level of isoprene plus the terpenes is 8.3×10^{14} μgC/yr (9×10^{8} metric ton/yr.). This number agrees reasonably well with the 4.38×10^{8} ton/yr value obtained by Rasmussen and Went (11).

The agreement of the emissions level for several species measured by different experimenters appears reasonable. For example, Tingey (25) measured emissions in an environmental chamber that enabled control of the light intensity and temperature. With live oak, Tingey found that the emissions are approximately 30 $\mu g\ g^{-1} hr^{-1}$. For slash-pine, Tingey obtained an average emission of approximately 5 $\mu g\ g^{-1}\ hr^{-1}$. Zimmerman gives an almost identical value of approximately 6 $\mu g\ g^{-1}\ hr^{-1}$. For loblolly pine, Arnts et al. (12)

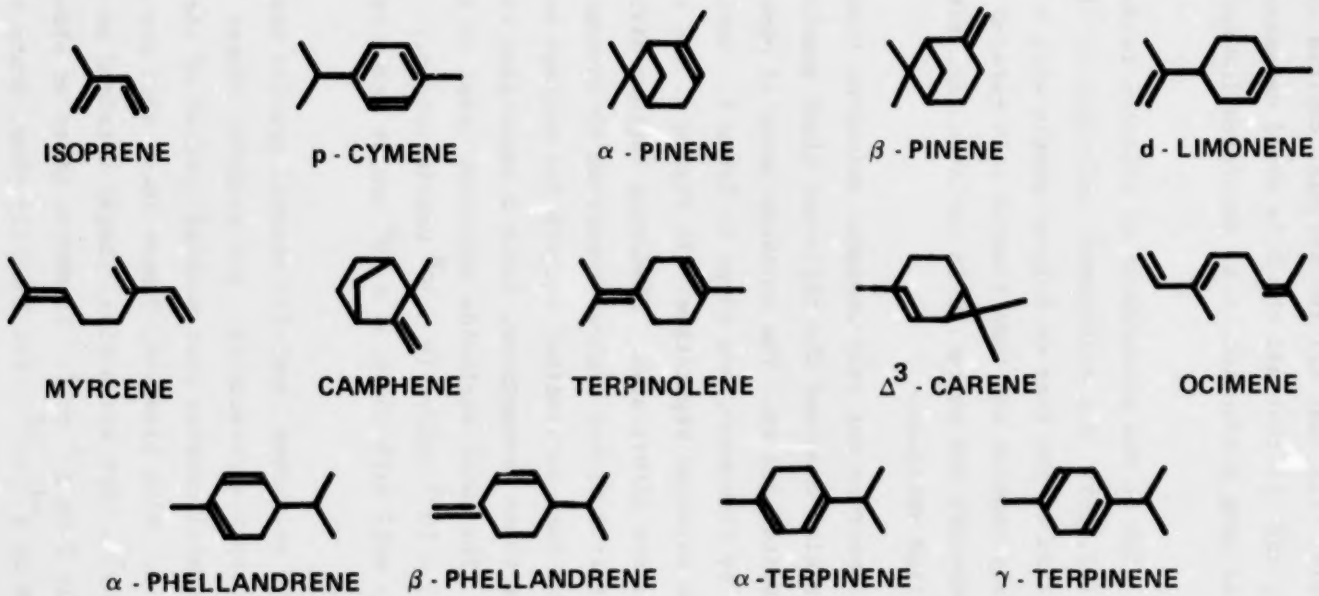

Figure 1. Structure of some selected natural hydrocarbons.

found an emission of 3 μg g^{-1} hr^{-1} at approximately 30°C in a North Carolina forest. The Arnts group measured a vertical profile of α-pinene over the forest, and by employing an energy balance equation (i.e., by measuring temperature, water vapor, carbon dioxide, and net solar radiation), they were able to calculate α-pinene flux values. The vertical gradient measurements for the α-pinene were difficult and could be subject to several errors. Assumptions of smooth terrain and constant wind fetch dimensions were also required.

Zimmerman, using the bag enclosure technique in North Carolina, obtained a value of 4.8 μg g^{-1} hr^{-1} for loblolly pine, which agrees favorably with the Arnts value. However, a reassessment of the Arnts study suggests that the proper wind fetch may not have been used. This error arose from a study of the H_2O and terpene vertical profiles.

TABLE 1. EMISSION RATES FOR SELECTED SAMPLES AT VARIOUS LOCATIONS

Sample Type	Emission Rate (μg g^{-1} hr^{-1})
Raleigh, NC (June 1977)	
Oaks	26.1
Shortleaf Pine	16.3
Loblolly Pine	4.85
Red Cedar	1.14
Virginia Pine	13.6
Pullman, Washington (August - November 1976)	
Ponderosa Pine	2.96
Mugo Pine	1.78
Douglas Fir	0.86
Juniper	3.25
Spruce	7.26
Pine litter	132.0*
Tampa, Florida (April - May 1977)	
Pasture	288.6*
Laurel Oak	11.2
Turkey Oak	26.2
Water Oak	27.2
Blue Jack Oak	16.5
All Oak species (night)	1.20

*The pine litter and pasture emissions are given in μg/m^2.hr. In order to convert the emissions shown for the vegetation from μg/g.hr to μg/m^2.hr, the biomass factors must be known. For the Raleigh, NC in June, the loblolly pine forest conversion factor is 709 μg/m^2 hr = 1 μg/g hr.

TABLE 2. MAJOR EMISSIONS FROM SELECTED SPECIES

Vegetation Type	Major Emissions*
Pullman, Washington	
Ponderosa Pine	36% Δ^3-carene
	25% β-pinene
	14% α-pinene
Lombardi Poplar (daytime)	99% Isoprene
Douglas Fir	24% α-pinene
	7% d-limonene
	5% β-pinene
Santa Barbara, California	
Eucalyptus (daytime)	40% Isoprene
Manzanita	18% Unknown 1
Chemise	25% Unknown 2
Research Triangle Park, NC	
Dogwood	10% Δ^3-Carene
Yellow Poplar	10% d-limonene
	8% Unknown 3
	5% Terpinolene
American Sycamore (daytime)	74% Isoprene
Eastern Red Cedar	52% Δ^3-carene
	26% α-pinene
Research Triangle Park, NC	
Loblolly Pine	35% α-pinene
	26% d-limonene
	19% β-pinene
	11% Δ^3-carene
Shortleaf Pine	53% α-pinene
	17% d-limonene
	12% β-pinene
	11% Δ^3-carene
Virginia Pine	26% Unknown 4
	22% α-pinene
	10% β-pinene
	8% d-limonene
	2% Δ^3-carene
Tampa, Florida	
All oaks (daytime)	90-99% Isoprene

TABLE 2. (Continued)

Vegetation Type	Major Emissions*
Long Leaf Pine	30% α-pinene 30% β-pinene 8% Propane
Slash Pine	27% α-pinene 19% d-limonene 16% β_3-pinene 12% Δ^3-carene
Sand Pine	44% α-pinene 35% β-pinene
Australian Pine (daytime)	92% Isoprene
Saw Palmetto (daytime)	85% Isoprene
Sabal Palmetto (daytime)	90% Isoprene
Cypress	46% α_3-pinene 21% Δ^3-Carene
Sweet gum	51% β-Phellandrene 20% Isoprene 13% α-pinene

*The sum of the emissions is not 100% since many small GC peaks were present and were not identified. Major unknown emissions are given with an assigned number.

The α-pinene levels determined by Arnts et al. (see Figure 2) should decrease linearly with the H_2O. However, α-pinene decreases with altitude above the canopy at a much higher rate. If one assumes that the H_2O measurements are correct, then the rapid decrease in terpene concentration can be a result of either α-pinene reactions with O_3, or insufficient wind fetch. Since the diffusion time of α-pinene for such small vertical distances is short, the terpene could not react significantly with O_3. One must conclude that the wind fetch was improper for suitable measurements, which indicates the Arnts flux value for α-pinene is too large.

The apparent agreement between the Arnts and Zimmerman studies suffers from another incompatability as well. Arnts found that 70-80% of the

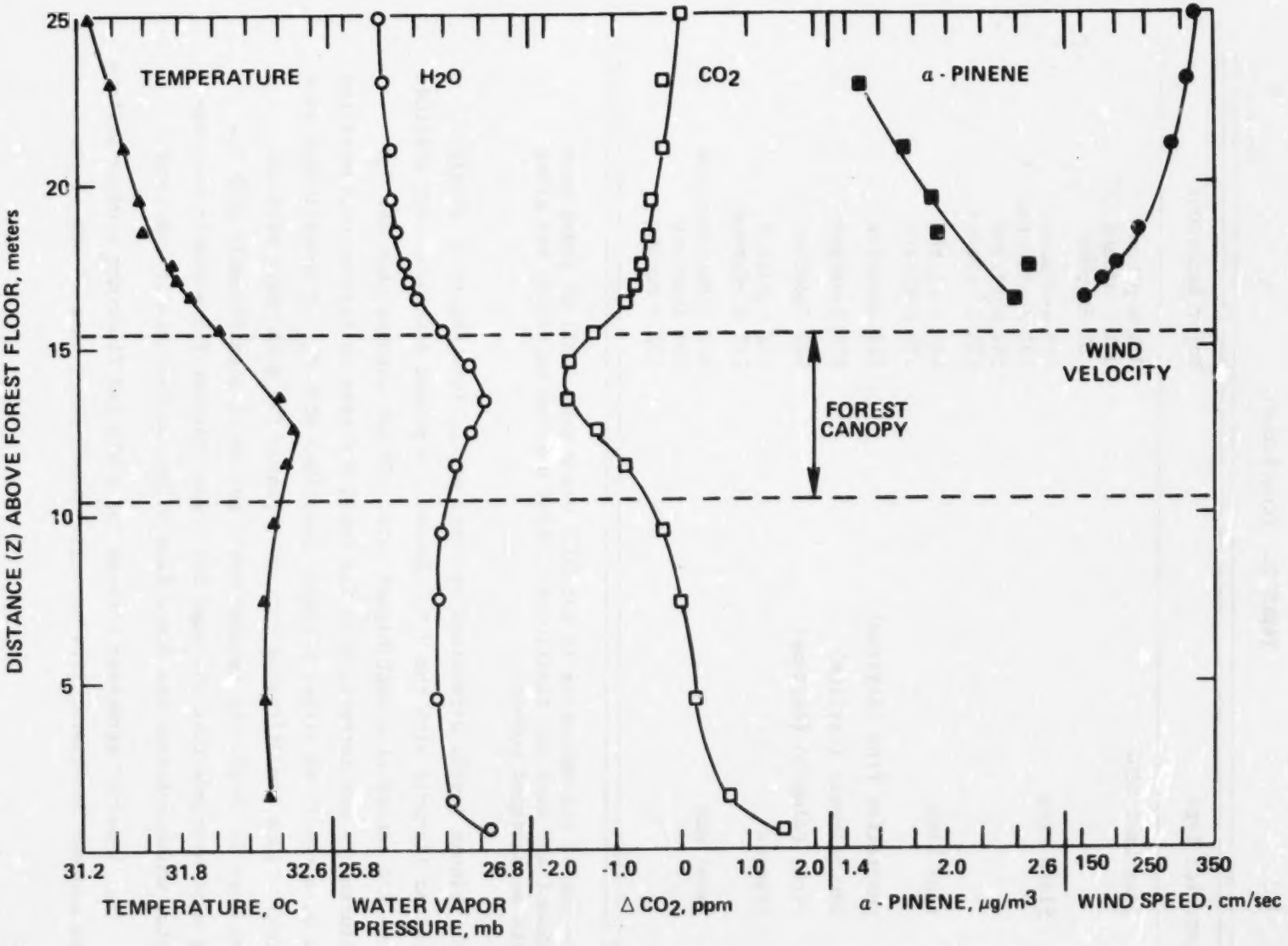

Figure 2. Loblolly pine forest vertical gradients, 7/18/77, 1035-1100 hrs e.s.t.

loblolly emissions are due to α-pinene. Zimmerman suggests 35%. The findings by Arnts are more compatible with the work of Mirov (26) in which the reported gum turpentine had a composition of 71% α-pinene and 22% α-pinene. If we assume the emissions to be proportional to the composition, the pine should liberate higher levels of α-pinene. Perhaps the disagreement in emission percentages rests on the two measurement techniques; Rasmussen (27) found the emissions from Mango foliage depend on the type of enclosure. Unenclosed, very little isoprene was liberated and the isoprene/n-butane ratio was quite small. However, when sheltered, the isoprene/n-butane ratio was greater, with isoprene increasing some forty-fold.

Rasmussen (28) recently suggested that the bag enclosure technique may not be a satisfactory way to measure emissions at least for deciduous-type vegetation. His unpublished work has shown that when a cylinder is placed over a tree branch and the emisisons are measured dynamically, the emissions levels are much lower. He suggests that perhaps the emissions are overestimated by as much as a factor of 10 with the bag-enclosure technique. If the Rasmussen findings prove correct, then the Zimmerman worldwide emission factor of 9×10^8 ton/yr must be revised downward. The Rasmussen position is consistent with the observations of Lonneman et al. (29), who calculated that at best only 5% of the total nonmethane hydrocarbon (TNMHC) in the Tampa St. Petersburg area could be attributed to natural emissions. In contrast, Zimmerman (30) calculated that 68% of the TNMHC is due to natural sources,a percentage based upon accurate anthropogenic emissions.

Of course, the above emission estimates could be in error. If the Lonneman estimate is correct for the Tampa St. Petersburg area, then the worldwide emission of natural HC's (isoprene and the terpenes) is not 9×10^8 ton/yr as suggested by Zimmerman, but closer to 10^6-10^7 ton/yr. This value is smaller by a factor of 10-100 than that originally proposed by Went, but is nonetheless more compatible with ambient air analyses. We shall see in a later section that the emission rates must be lower than those given by Zimmerman, since air quality data do not substantiate high emission values.

TABLE 3. ESTIMATED U.S. AND GLOBAL EMISSIONS BY LATITUDE (gC/yr)

Latitude U.S.	Isoprene	Terpenes
45-50°	1.8×10^{11}	4.6×10^{12}
40-45°	5.8×10^{11}	1.0×10^{13}
35-40°	4.3×10^{12}	1.6×10^{13}
25-35°	1.5×10^{13}	1.9×10^{13}
Global (temperate)	9.6×10^{13}	2.3×10^{14}
Global (tropical)	2.5×10^{14}	2.5×10^{14}
Total Global	3.5×10^{14}	4.8×10^{14}

SECTION 5

REACTIVITIES OF NATURAL HYDROCARBONS

The suggestion has been made that natural HC's are not observed in high concentrations in the atmosphere since they, being mostly olefinic react very quickly with the OH and O_3 usually present in the ambient air (31, 32). Qualitatively this premise is correct. Biogenic HC's, like all organic compounds (including methane), will participate in OH ractions. If the compounds are olefinic, they will also participate in O_3 reactions. Rate constants for some selected natural HC's are shown in Table 4.

Went (10) suggested that natural HC's react with ozone in the atmosphere to produce aerosols since a blue smoke appeared when ozone and crushed pine or fir needles were placed into a jar. In a later publication, Went suggested that a large portion of condensation nuclei present in the atmosphere is a direct result of photochemical reactions similar to those responsible for the production of photochemical smog. Stephens and Scott (39) studied the photooxidation of monoterpenes, specifically pinene and α-phellandrene, when investigating the relative reactivities of a number of HC's. The found α-phellandrene to be very reactive at a rate slightly greater than tetramethyl-ethylene. The pinene was about six times slower in reactivity, but slightly faster than isobutene. The pinene isomer studied is not given.

Ripperton et al. (14) studied the α-pinene/ozone reaction, in which they noted the production of aerosols. Although a second-order rate constant is given (0.24 ppm^{-1} min^{-1}), the experimenters found that much more α-pinene reacted than ozone. In two replicate runs, the α-pinene/O_3 consumption ratio was approximately 2/1 and over 3/1, respectively. The work suggested that a reactive product is produced (free radicals) that will react further with the α-pinene.

TABLE 4. RATE CONSTANTS FOR SELECTED HC's

Compound	Reactant	Rate Constant (ppm^{-1} min^{-1})	Reference
n-Butane	O_3	slow	--
	OH	3.5×10^{3}	NBS (33)
Propylene	O_3	1.6×10^{-2}	NBS (33)
	OH	3.8×10^{4}	NBS (33)
Isoprene	O_3	1.9×10^{-2}	Arnts (34)
	OH	1.2×10^{5}	Winer (35)
Trans-2-Butene	O_3	0.39	NBS (33)
	OH	1.0×10^{5}	Atkinson (36)
α-Pinene	O_3	2.1×10^{-1}	Grimsrud (37)
	OH	1.2×10^{5}	Winer (35)
β-Pinene	O_3	5.8×10^{-2}	Grimsrud (37)
	OH	9.8×10^{4}	Winer (35)
d-Limonene	O_3	0.96	Grimsrud (37)
	OH	2.1×10^{5}	Winer (35)
Myrcene	O_3	0.18	Grimsrud (37)
	OH	3.4×10^{5}	Winer (35)
3-Carene	O_3	0.18	Grimsrud (37)
	OH	1.3×10^{5}	Winer (35)
p-Cymene	O_3	6×10^{-7} *	Pate (38)
	OH	2.3×10^{4}	Winer (37)
α-Phellandrene	O_3	1.7	Grimsrud (35)
	OH	--	--
ß-Phellandrene	O_3	2.6×10^{-1}	Grimsrud (35)
	OH	1.7×10^{5}	Winer (37)

* This rate constant is for p-xylene but p-cymene should have a rate constant very similar to xylene.

Lillian (40) also studied α-pinene reactions, but in the presence of NO_x. He found that irradiated α-pinene/NO_x mixtures produced the same characteristics as photochemical smog, i.e., the reaction of HC's, the

oxidation of NO to NO_2, and the production of ozone. Alpha-pinene was also found to act as both a source and a sink for ozone, and to be a source of light-scattering aerosols.

The most complete study on the reactivities of monoterpenes is the work of Grimsrud et al. (37). These investigators studied the reactions of natural HC's with ozone and with NO_x. The compounds investigated were; p-menthane, p-cymene, α- and β-pinene, isoprene, 3-carene, α - and β-phellandrene, γ -terpinene, carvomenthene, limonene, myrcene, cis-ocimene, terpinolene, and α-terpinene. Isobutene was also studied as a reference organic compound.

In general, compounds with high ozonolysis rates also have very high photooxidation rates. Grimsrud et al. found that all the HC's except ocimene and terpinolene showed 1:1 stoichiometry with ozone. Ocimene is a triolefin and ozone is expected to react with more than one double bond. Terpinolene showed 1:2 stoichiometry due to the presence of two double bonds, but only at high O_3/HC ratios.

The photooxidation of four C_{10} terpenes in the presence of NO_x was investigated by Westberg (41). The four terpenes were: limonene, α-pinene, terpinolene, and ocimene. In each compound the amount of ozone produced was found to be dependent upon the HC/NO_x ratio. Westberg's data are shown in Figure 3 for the two levels of NO_x. The curves show that the optimum ozone varies somewhat for different terpenes. The maximum ozone is produced between the 13/1 ratio for terpinolene (NO_x = .05 ppm) and the 28/1 ratio for limonene (NO_x = 0.20 ppm). Higher ozone levels were observed with more NO_x, probably as a result of further photooxidation of the initial reaction products. Interestingly, the ozone maximum shifts to the higher HC/NO_x ratio at the higher initial NO_x concentration. For terpinolene, 0.05 ppm NO_x, the O_3 maximum occurs at a HC/NO_x ratio of 13; at 0.2 ppm NO_x, the maximum is observed at a ratio of 22. For the limonene, the O_3 maxima occur at HC/NO_x ratios of 21 and 28 for the 0.02 and 0.5 ppm NO_x. This effect is probably a result of the rapid reaction between olefins and ozone, since it was not observed with a n-butane/NO_x system (42).

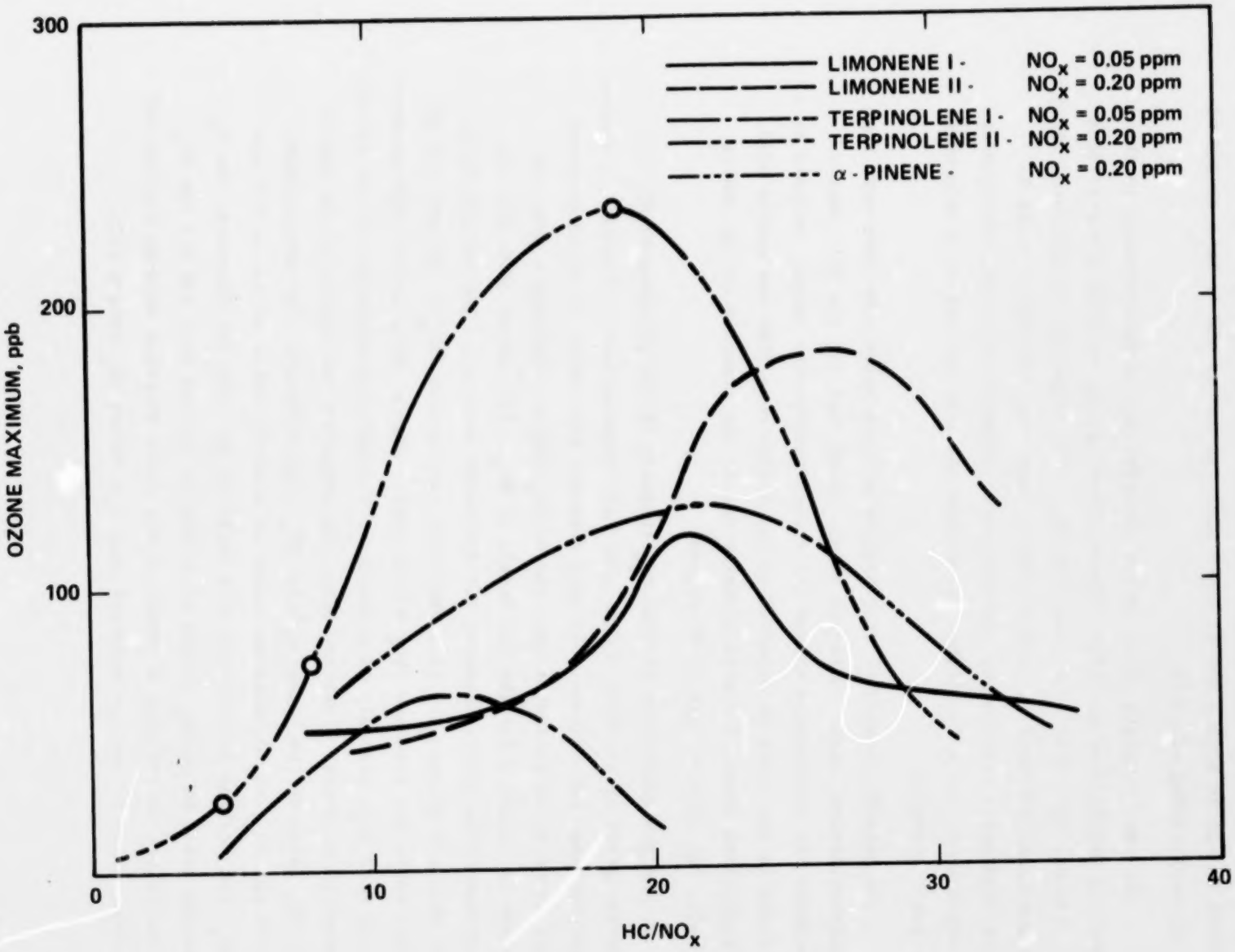

Figure 3. Ozone prodiction as a function of HC/NO_X.

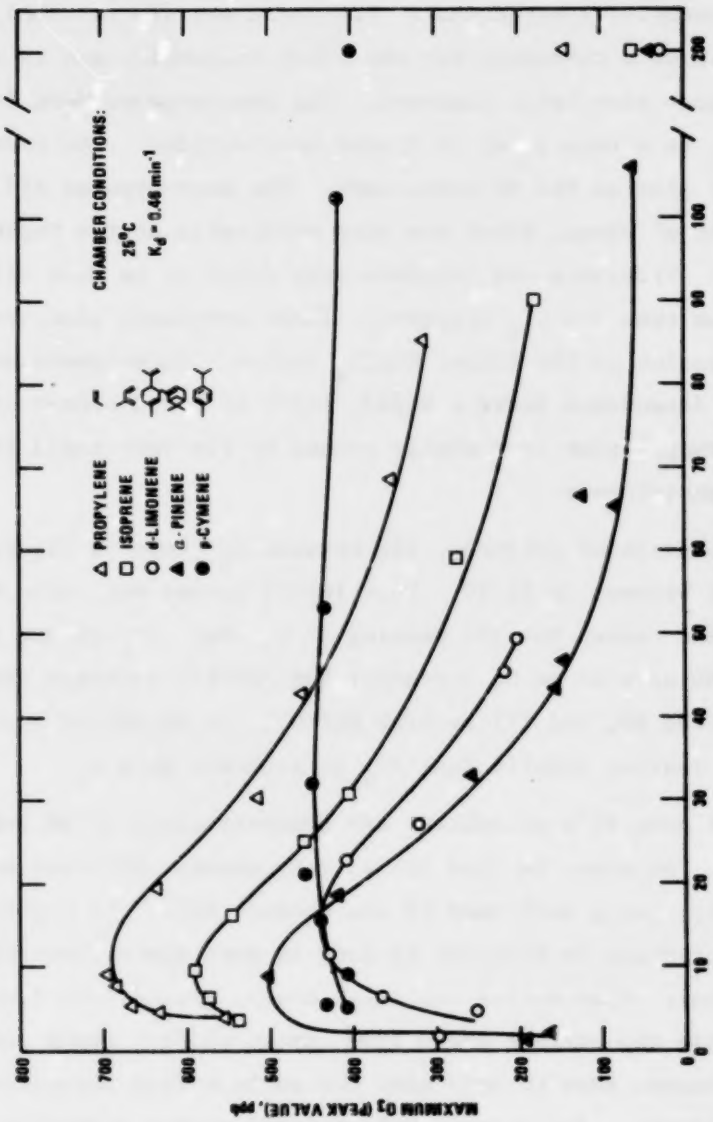

Figure 4. Effect of hydrocarbon to NO_x ratio on ozone maximum.

Arnts and Gay (34) investigated the reactivities of six $C_{10}H_{16}$ monoterpenes, a $C_{10}H_{15}$ aromatic, and a C_5H_8 diolefin. The terpenes were myrcene (acyclic triolefin), d-limonene and terpinolene (monocyclic diolefins), α- and β-pinene, and Δ^3-carene (bicyclic monolefins). The aromatic studied was p-cymene (p-isopropyl toluene), while the C_5 diolefin was isoprene (2-methyl-1,3-butadiene). Propylene was also studied because this olefin serves as a reference for the other compounds, and is often used to test chamber reactivity compound. The monoterpenes were found to oxidize NO to NO_2 at a rate equal or faster than propylene. The aromatic p-cymene was very slow in the NO conversion. The monoterpenes did not permit the buildup of ozone, which was very noticeable at the higher HC/NO_x ratio (Figure 4). Propylene and isoprene were found to be more efficient in producing ozone than the C_{10} terpenes. These compounds also showed some ozone suppression at the higher HC/NO_x ratios. Para-cymene showed almost no HC/NO_x dependence above a HC/NO_x ratio of 3 and almost no reaction with O_3. Ozone suppression is probably caused by the very rapid reaction of O_3 with the monoterpenes.

With the exception of p-cymene, the maximum O_3 shown in Figure 4 is observed to occur between 10 to 20. This result agrees well with Westberg (41). The probable causes for the peaking of O_3 are: (1) at the initial low HC/NO_x, the NO acts as an O_3 scavenger and quickly titrates any O_3 produced with excess NO, and (2) at high HC/NO_x, the excess HC reacts very quickly with O_3, leaving insufficient NO_x to generate more O_3.

Lifetimes of some HC's at ambient air concentrations of OH and O_3 are given in Table 5. As shown in this table, many natural HC's are expected to oxidize quickly, along with many of the manmade HC's. At night, the OH radical concentration is expected to drop to zero since these radicals are light dependent. Also during nighttime hours, ground base temperature inversions decouple the surface ozone from layers aloft. Ozone concentration consequently decreases even to zero near the surface from deposition losses and chemical reactions. The natural HC's emitted during nighttime are thus expected to persist until the following day. However, isoprene is not emitted at night and monoterpene emissions are minimal at night, since the temperature

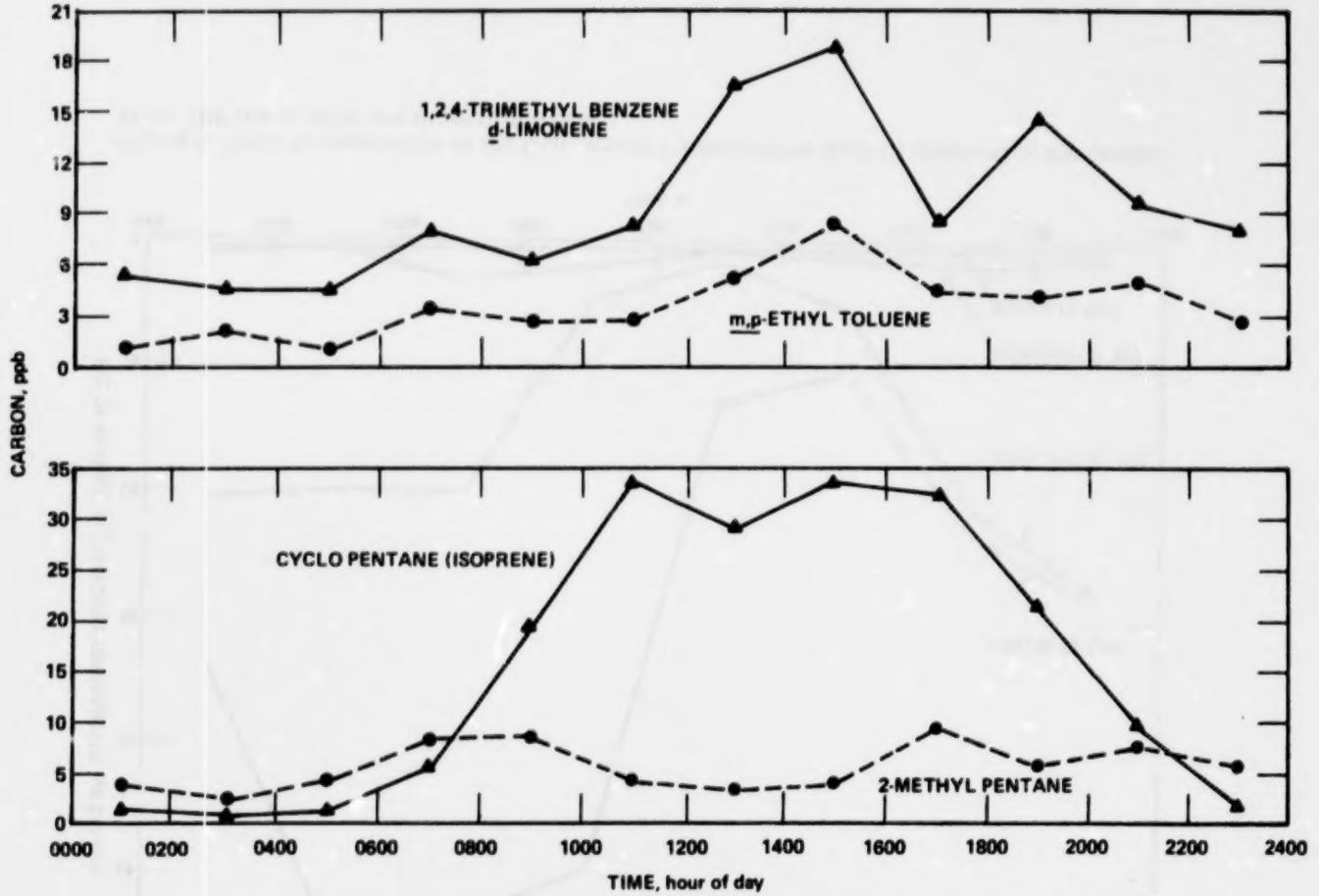

Figure 5. Diurnal variation of hydrocarbon compounds, Chickatawbut Hill, July 18,1975.

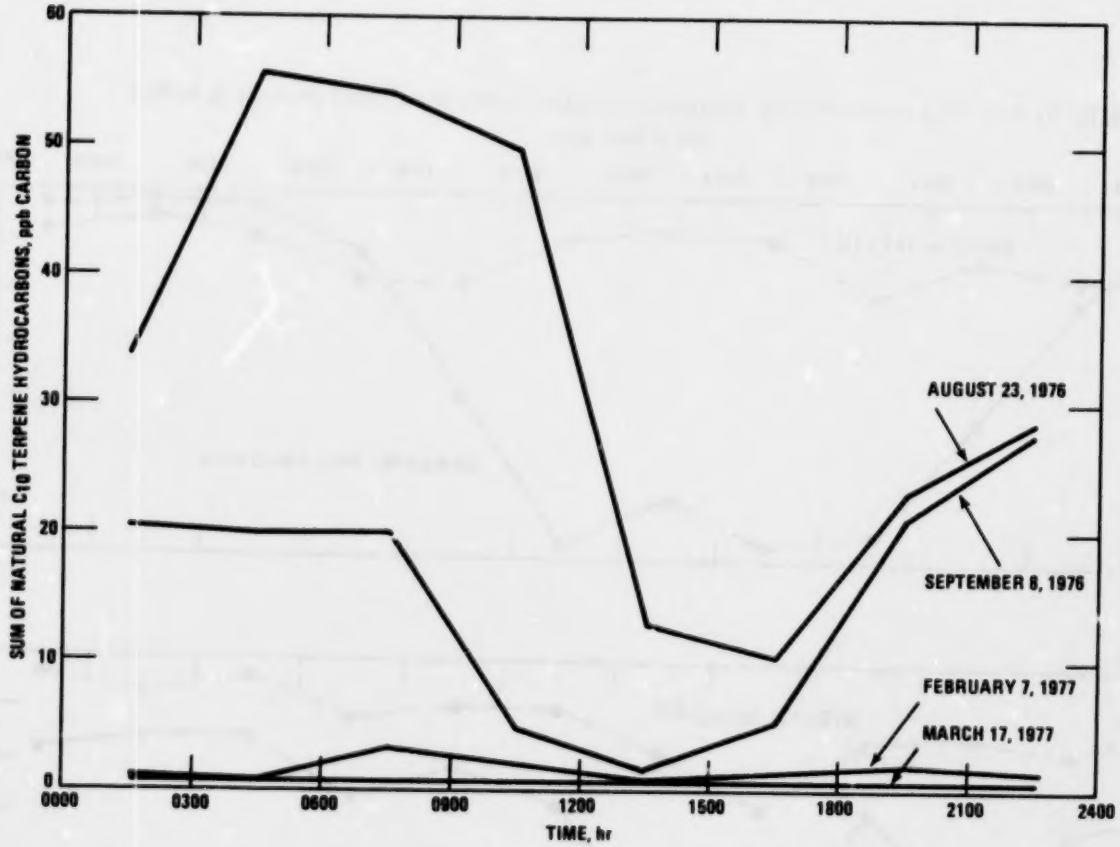

Figure 6. Total concentration of the C_{10} terpene hydrocarbons (ppb C) observed in the canopy at the IBP site at different times of the year.

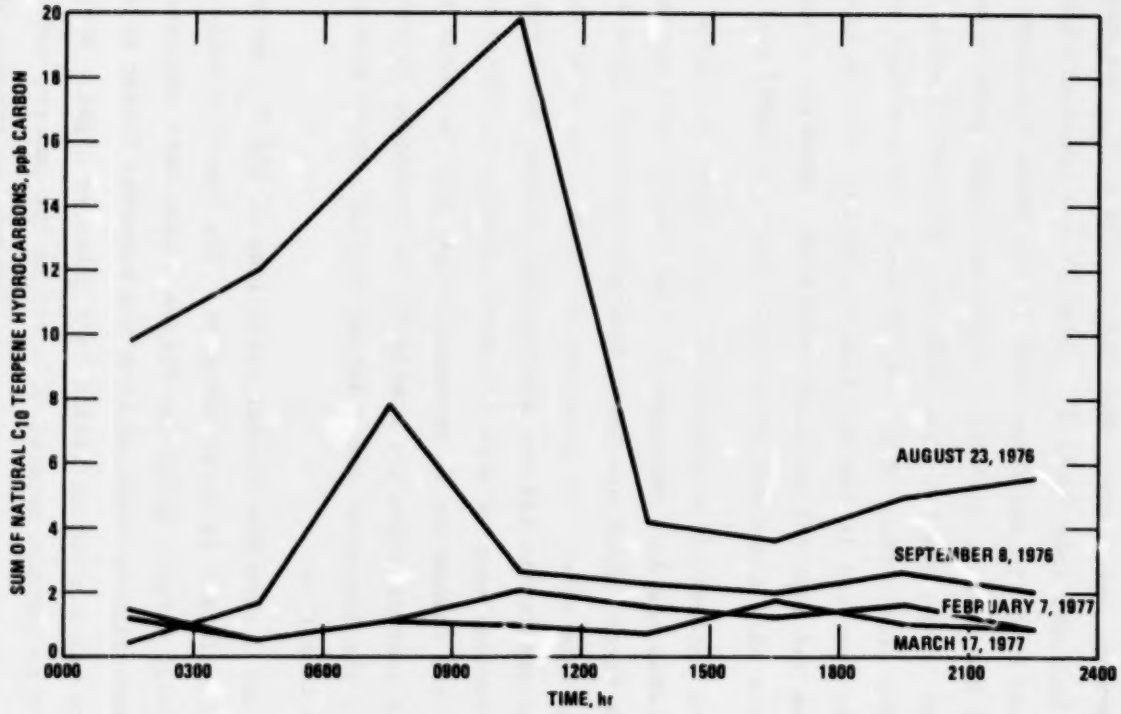

Figure 7. Total concentration of the C_{10} terpene hydrocarbons (ppb C) observed above the canopy at the IBP site at different times of the year.

is lower. Table 5 shows that some natural HC's can be expected to survive the attack of OH and O_3 long enough to be observed in the ambient air, especially p-cymene. However, the amount of natural HC's observed in ambient air analyses is very low.

Data obtained in a number of cities, including Tampa/St. Petersburg, Miami, Tulsa, Houston, and Boston, show practically no C_{10} natural HC's and very little isoprene (see Table 6). Similar low concentrations of natural HC's were obtained by Arnts and Meeks (43) in the Smoky Mountains of Tennessee and in Rio Blanco, Colorado. Arnts and Meeks found a maximum of 5.7 ppbC isoprene in the Smokies when TNMHC was 102 ppbC; isoprene was found at 5.6 ppbC in Rio Blanco when TNMHC was 117 ppbC. No α-pinene or other terpenes could be detected in the Rio Blanco samples. In the Smoky Mountain samples, p-xylene and α-pinene were not separated. However, their combined concentration was only a maximum of 2.5 ppbC when the TNMHC was 171 ppbC.

Some diurnal variations of natural HC's are shown in Figure 5,6 and 7. Figure 5 illustrates the data obtained at Chickatawbut Hill southwest of Boston. Red oak trees, which are known isoprene emitters, grow in the area surrounding this site. The isoprene in Figure 5 is shown with cyclopentane since GC separation did not distinguish between these two HC's. However, since roadway samples show 3/1 ratio between cyclopentane and 2-methyl-pentane, the assumption is reasonable that the increases in cyclopentane/isoprene concentration are mostly due to increases in isoprene--especially since the increases occur during daylight hours when deciduous-type vegetation is active.

Figures 6 and 7 show the diurnal variations of the C_{10} terpenes found at a loblolly pine forest in North Carolina. The Figure 6 data were taken within the loblolly forest, while the Figure 7 data were obtained 5 m above the canopy. These figures contrast with the hardwood forest at Chickatawbut Hill in that the terpene concentration is highest at night. Noctural inversions serve to contain natural HC's within the canopy, and pine emissions are not directly affected by the presence or absence of sunlight. Also shown in these figures is the large difference in concentration between summertime and wintertime. Of note is that just 5 m above the

canopy the natural HC's dropped to one third of the concentration within the canopy. On August 23 of the study, the biogenic contribution to the TNMHC was 40% in the canopy. At 5 m above the canopy, the biogenic contribution is just 12%.

TABLE 5. HALF-LIFE IN HOURS FOR SELECTED HC's AT VARIOUS OZONE CONCENTRATIONS[a]

	Ozone Concentration (ppb)						
Compound	0	30	50	80	100	150	200
n-Butane	165	Same	Same	Same	Same	Same	Same
Propylene	15.2	9.31	7.40	5.66	4.80	3.65	2.92
t-Butene-2	5.61	0.86	0.55	0.36	0.29	0.19	0.14
Isoprene	4.81	4.16	3.40	2.96	2.68	2.22	1.86
α-Pinene	4.81	1.32	0.89	0.60	0.49	0.39	0.26
d-Limonene	2.75	0.35	0.22	0.14	0.12	.09	0.07
Myrcene	1.72	0.19	0.12	.09	0.07	0.05	0.03
β-Pinene	5.88	3.26	2.37	1.75	1.48	1.08	0.85
3-Carene	4.44	1.4	0.99	0.68	0.56	0.39	0.29
p-Cymene	25.1	Same	Same	Same	Same	Same	Same
β-Phellandrene	3.39	1.03	0.70	0.47	0.39	0.27	0.21
Toluene	63.5	Same	Same	Same	Same	Same	Same
m-xylene	16.5	Same	Same	Same	Same	Same	Same

[a] OH concentration = 2×10^{-8} ppm

A summary of the ambient air measurements is given in Table 7, showing that the highest values are recorded by Rasmussen and Went (11) and by Whitby and Coffey (46). High-resolution GC columns were not available at the time of the Rasmussen and Went (11) study, and many unidentified GC peaks were assumed to be natural HC's in the Whitby and Coffey report. They made this assumption largely because the samples were collected in farmland areas. Indeed, if both of these studies are excluded from the table, the average isoprene concentration measured in ambient air lies between 0.1 and 10 ppbC, while the predominate monoterpene, α-pinene, lies between

TABLE 6. HC's FOUND NEAR SEVERAL CITIES (PPB V/V)

Compound	Sub-urban Tampa/St. Petersburg (5-14-76)	N. Sub-urban Miami (5-16-76)	Tulsa (7-27-78)	Houston (4-2-74)	S.Sub-urban Boston (7-31-75)
Ethane	3.0	5.7	11.6	41.8	3.6
Ethylene	3.8	10.5	11.5	78.2	INT
Propane	3.1	19.5	15.5	63.9	6.2
Acetylene	4.6	11.3	8.4	7.7	4.2
Isobutane	2.5	5.5	8.1	39.7	4.1
n-Butane	7.5	16.4	16.5	71.1	9.6
Propylene	0.9	--	4.2	27.9	1.4
Isopentane	9.0	22.3	17.3	77.4	11.6
n-Pentane	4.0	10.2	12.1	42.8	6.3
Isobutylene	1.3	2.6	1.2	21.0	1.9
T-Butene-2	0.6	2.2	1.6	1.8	0.9
C-BuT-2-Butadiene	1.3	--	--	2.5	1.6
Pentene-1	0.1	0.7	0.8	1.3	0.6
2-Mebutene-1	0.3	--	0.6	2.1	trace
T-Pentene-2	--	1.8	-	9.6	trace
C-Pentene-2	--	2.1	-	1.7	--
2-Mebutene-2	--	-	-	1.6	--
Cyclopentane + Isoprene	5.1	2.8	3.6	36.5	2.3
2-Mepentane	3.0	6.5	6.3	*	6.3
3-Mepentane	1.8	4.0	4.5	24.9	4.2
4-Mepentene-2	0	0.1	-	0.0	--
n-Hexane	1.7	3.1	6.1	27.9	4.7
Hexene-1	0.1	0.1	0.41	--	--
T-Hexene-3	0.3	0.1	--	--	0.2
2,4 Dimepentane	1.9	.2	5.1	1.1	0.5
Mecyclopentane	--	--	-	12.4	2.5
CIS-Hexene-2	--	--	-	--	--
Unknown	--	--	-	--	--
3,3 Dimepentane	--	--	-	--	--
Cyclohexane	--	--	1.8	--	0.7
2 Mehexane	-	--	5.0	20.5	2.3
2,3 Dimepentane	--	--	3.3	7.8	1.0
3 Mehexane	1.6	--	5.7	3.5	1.8
1C3 Dimecypentane	--	--	1.02	10.2	--
2,2,4 Trimepentane	1.3	1.5	4.6	14.7	1.0
1T3 Dimecypentane	--	--	2.02	--	--
n-Heptane	1.1	1.5	6.12	13.3	1.5
Mecyclohexane	4.3	1.2	6.68	15.8	0.6
Toluene	7.2	6.1	16.8	90.5	24.2
Unknown	15.1	0.6	--	--	--
Unknown	16.4	0.4	--	--	--
Nonane	2.8	0.4	1.9	6.6	3.3
Unknown	--	--	--	--	--

TABLE 6. (CONTINUED)

Compound	Sub-urban Tampa/St. Petersburgh (5-14-76)	N. Sub-urban Miami (5-16-76)	Tulsa (7-27-78)	Houston (4-2-74)	S.Sub-urban Boston (7-31-75)
Ethylbenzene	1.4	1.4	2.59	13.0	2.3
P-Xylene	1.2	2.6	1.6	28.2	2.3
M-Xylene	3.3	--	5.3	36.7	7.3
Unknown	0.5	0.5	--	--	--
α-Pinene	--	--	--	--	--
O-Xylene	4.1	--	3.3	14.6	4.8
Unknown	--	--	--	--	2.0
Isopropyl benzene	1.4	--	--	28.5	1.1
N-Decane	--	--	2.3	11.2	--
β-Pinene	--	--	--	--	--
N-Propylbenzene	0.6	1.0	--	2.7	0.8
M-Ethyltoluene	1.4	0.4	3.3	10.6	3.1
Δ-Carene	--	--	--	--	--
1,3,5 Trimebenzene	0.8	0.6	1.92	4.3	1.0
O-Ethyltoluene	--	1.4	--	1.0	0.3
1,2,4 Trimebenzene	0.9	--	2.1	11.6	6.0
Unknown	--	--	--	4.0	--
D-Limonene	--	--	--	--	--
p-Diethylbenzene	--	--	--	5.9	--

* Measured with 3-methyl pentane

less than 0.1 to 14 ppbC. It is not clear why Cronn and Harsch (51) observed such high concentrations of Δ^3-carene in the Smoky Mountains. From Table 2, it is noted that ponderosa pine, dogwood, eastern red cedar, loblolly pine, shortleaf pine, Virginia pine, slash pine, and cypress all emit Δ^3-carene. However, this area contains; Canada hemlock, eastern hemlock, pitch pine, white ash, yellow buckeye, sugar maple, basswood, yellow birch, yellow poplar, American beech, mountain silverbell, black cherry, mountain laurel, northern red oak, rhododendron, and cucumber tree. We suspect that Δ^3-carene has been misidentified. This is especially suspect since only one aromatic toluene was identified and high values of Δ^3-carene were observed when the acetylene concentration was also high. This suggests that the samples were contaminated with auto exhaust, assuming acetylene as properly identified.

TABLE 7. Summary of Biogenic HC Concentrations in Ambient Air

Investigator-Sampling location(s)	Surrounding vegetation	Biogenic hydrocarbon	Avg. Conc. ppbC	Max ppbC	Min ppbC	TNMHC ppbC	% biogenic	% automotive	Comments
Rasmussen & Went (11) Ozark Plateau, MO	Hardwood forest & prairie	Isoprene	totaled	150	70				Lowest levels observed just before sunrise; high levels observed when deciduous foliage changes color in the autumn; high level of volatiles observed after grass was mowed; packed column GC-FID
		α-pinene				--	--	--	
		β-pinene	106						
		limonene							
		myrcene				--	--	--	
Gray Summit, MI	Junipers &	totaled	41	60	30	--	--	--	
Highland Biological St.MC	Hardwood forest	totaled	50	120	10	-	-	--	
Gray Summit, MI	Hardwood forest meadow	totaled	109	340	10	-	--	--	
Rasmussen, et.al. (44) Elkton, MI	Hardwoods & farmland	Isoprene	6	28	0	98	6	12	79 measurements; most intensive study yet performed,GC - FID high resolution SCOT column
Lonneman et.al. (45) Chickatawbut Hill, MA	Oak & other	isoprene	10(1 day)	34	1				SCOT column
Whitby & Coffey (46) Adirondack Mountains,NY	Coniferous forest	'terpene species'	33	72	5.3	-	--	--	Chromatographic peaks not identified; authors assumed biogenic origin due mainly to rural location; packed column GC-FID.
		'lighter species'	63	123	29.3	--	--	--	
	Deciduous/ coniferous forest	'terpene species'	12	17	6.5	--	--	--	
		'lighter species'	18	21	14	--	--	--	
Lonneman, et.al. (29) St. Petersburgh/Tampa, Miami and the Everglades, Florida	Orange groves, gum cyprus, oak, wax myrtle, black Willow, persimmon	isoprene	1.61	4.5	0.1	106	4 (max)	61	gc-fid; WCOT columns
		d-limonene	0	--	--	--			
		α-pinene	0	--	--	--			
		β-pinene	0	--	--	--			

TABLE 7. (Continued)

Investigator-Sampling location(s)	Surrounding Vegetation	Biogenic Hydrocarbon	Avg. Conc. ppbC	Max ppbC	Min ppbC	TNMHC ppbC	% Biogenic	% Automotive	Comments
Schjoldager & Wathue (47) Gjerdrum, Norway	Coniferous forest (spruce & farmland)	α-pinene	14.0	16.5	10.5	--	--	--	High resolution glass capillary column used; 3 data points
		β-pinene	9.5	19.5	3.0	--	--	--	
		limonene	--	trace	--	--	--	--	
		isoprene	--	--	<0.5	--	--	--	
Seila (48) Jones State Forest, (38 mi North of Houston, TX)	Loblolly pine	α-pinene	3.6	7.7	<0.1	357	2	12	GC-FID; SCOT
		isoprene	0.1	1.2	<0.1				
Holdren, et.al (49) Moscow Mountain, North-Central Idaho	Coniferous forest (pine and fir)	α-pinene	1.13	7.3	0.1	--	--	--	Samples collected outside the forest contained no measurable terpenes (less than 0.1 ppbC) with single ion peak monitoring
		β-pinene	0.86	4.6	<0.1				
		3-carene	0.64	5.4	<0.1				
		limonene	0.10	0.5	<0.1				
		α-pinene	1.23	2.7	0.3				
		β-pinene	1.73	5.7	<0.1				
		3-carene	1.08	3.7	<0.1				
		limonene	0.10	0.2	<0.1				
Arnts & Meeks (43) Tulsa (Suburban) OK	Deciduous Farmland	Isoprene*	0.45	1.16	<0.1	423	0.1	36	GC-FID; WCOT columns
Rio Blanco, CO	Sage Brush, coarse grass, juniper, pine	Isoprene	2.10	5.63	<0.1	377	1.6	27	GC-FID; WCOT columns
Smokey Mts., TN	Deciduous Coniferous	Isoprene†	3.84	5.72	0.1	117	4.1	42	GC-FID; WCOT columns
		α-pinene	--	--	--	--	--	--	
Air Resources Board (50) Lake Tahoe High School CA	Pine	α-pinene	9.2	13.4	4.3	123	9.2	--	GC-FID
		β-pinene	3.9	8.6	0.2	123	3.9	--	GC-FID
Cronn - Harsch (51) Smoky Mts TN	Deciduous Coniferous	Isoprene	4	17.4	†				
		α-pinene	3.9	7.9	1.2	88.2	21	--	GC-FID WCOT column
		β-pinene	2.5	3.1	1.2				
		Δ^3-carene	7.34	20.8	1.1				
		Myrcene	1.76	2.0	--				

* Other natural hydrocarbons could be identified if concentrations exceed 0.1 ppbC

† Alpha-pinene is shown with p-xylene, maximum concentration of both is 2.44 ppbC.

The automotive contribution shown in Table 7 was obtained by employing the Lonneman method (52). This method uses the TNMHC/acetylene ratio for tunnels. With this ratio and knowledge of the acetylene concentration of the ambient air sample, an automotive contribution can be calculated. The Cronn and Harsch samples contained very high acetylene concentrations making the calculated automotive contribution greater than the total observed non-methane hydrocarbon concentration in most samples. Either the acetylene or the TNMHC concentration is in error. There is also the possibility that some of the acetylene could arise from the burning of wood at camp sites nearby (53). This would invalidate the Lonneman method for calculating automotive contribution to TNMHC.

As stated earlier, isoprene, α-pinene and most certainly p-cymene have lifetimes that are long enough for observation if their emissions are high, even though their reactivity is also high. But p-cymene was not observed at all, though isoprene and α-pinene were observed at very low levels. Also, the natural HC contribution to the TNMHC in the Smokies was found to be very low -- usually less than 5% (43). The maximum values for isoprene and α-pinene obtained for the 7-day study (September 21-27, 1978,) were 5.72 ppbC and 1.17 ppbC, respectively, but were not recorded on the same day. If the Cronn and Harsch work is considered the natural hydrocarbon contribution is still only ~ 20% of the total hydrocarbon burden. Also the TNMHC is only ~ 90 ppbC. This is still a low percentage considering the fact that the area is surrounded with vegetation.

SECTION 6

PRODUCT FORMATION

As discussed earlier, a number of studies have shown that natural HC's can produce aerosols when undergoing ozonolysis or photooxidation in the presence of NO_x. Went, who first observed a blue haze by placing O_3 and pine needles in a bell jar (10), further suggested that the mechanisms for removal of natural HC's are similar to those responsible for smog formation. In his dissertation work, Rasmussen studied some terpene reactions with O_3 and NO_2 (54). Though he was unable to analyze the aerosol material resulting from reaction, he did point out that the products consisted of compound s both lighter and heavier than the parent compound.

Isoprene was included as one of the HC's studied by Schuck and Doyle (2). When 3 ppm isoprene were irradiated with 1 ppm NO_x, the products observed were 1.7 ppm formaldehyde, 0.90 ppm CO, 0.20 ppm peroxyacetylnitrate (PAN), 2.7 ppm acetaldehyde and 1.2 ppm acrolein. These investigators were able to account for approximately 87% of the reacted carbon as identifiable products.

When 5 ppm of both pinene and phellandrene were irradiated with 5 ppm NO_2, Stephens and Scott (39) found that 0.25 and 0.23 ppm PAN was produced. Pinene also produced 1.3 ppm aldehyde, while phellandrene produced 2.0 ppm. If formaldehyde is taken as the aldehyde product, then only 4.6 and 6.1% of the carbon is accounted for, assuming all the initial HC reacts.

Haze formation was studied in New York City and the Blue Ridge Mountains by Wilson et al. (55). They also synthesized aerosol production in an environmental smog chamber, and collected the aerosols produced from the photooxidation of α-pinene by extraction and derivation techniques. Gas chromatograms and mass spectra of the extracted compounds indicated the presence of pinonic acid and norpinonic acid.

In a later study on haze formation also involving photooxidation of α-pinene in a smog chamber, Schwartz (56) was able to identify an additional product, pinononic aldehydes, in the neutral fraction. Pinonic and pinononic acids were observed in the acid fraction of the extraction, but in the base fraction, too little sample was available for analyses. The aerosols collected at the Smoky Mountain site also contained the two acids. The experimenters concluded from this study that the blue haze is a photochemical aerosol fueled in part by the terpene emissions from trees. Unfortunately, since no quantitation of the aerosol composition was attempted, one cannot quantitate the degree of visibility reduction resulting from terpene oxidation. One would expect in light of recent findings that the contribution of natural HC's to visibility reduction is minimal (57, 58).

Weiss et al. (57) measured sulfates in submicron aerosols at several locations. In the Ozarks, carbon species, not sulfates, were determined to dominante the haze-producing aerosols. Stevens (58) made similar observations in the Smoky Mountains in a study in 1978.

Arnts and Gay (34), in their study on the chemistry of natural HC's, tried to identify products arising from the photooxidation of the HC's with NO_x. They studied isoprene, myrcene, d-limonene, terpinolene, α, and β-pinene and Δ^3-carene. The major gaseous products observed with the long-path Fourier transform system-infrared (FTS-IR) are given in Table 8. The products include, CH_2O, HCOOH, CO, CO_2, CH_3CHO, PAN, and $(CH_3)_2CO$. Methyl vinyl ketone and methacrolein were also observed as derivation products of isoprene.

Isoprene showed the highest product accountability (24% of reacted carbon); the remaining compounds showed gaseous products from 2 to 17% of the reacted carbon. Several unidentified absorption bands were also detected, suggesting additional products. Using reasonable absorption coefficients, however, the amount of material attributable to the unidentified compounds is not very large. GC analyses performed by Arnts and Gay detected only a small amount of acetaldehyde, although the GC system was able to detect hydrocarbons to C_{12}. No other products eluted from the GC column.

TABLE 8. REACTIVITY AND PRODUCTS BY FOURIER TRANSFORM SPECTROSCOPY (LONG-PATH INFRARED) AT 60 MIN[a]

Compound	HC/NO_x Ratio	%HC Reacted	H_2CO	HCOOH	CO	CO_2	CH_3CHO	PAN	$(CH_3)_2CO$	%ACC
β-Pinene	5.3	58	0.94	0.39	0.23	0.4	0.05	0.018	0	2.1
Δ-Carene	6.7	60	0.46	0.39	0.50	0.9	0.33	0.26	0	7.1
Isoprene	6.2	68	2.39	0.44	0.77	0.2	2.0	0.32	0	24.8
α-Pinene	6.7	72	0.33	0.32	0.39	0.6	1.57	0.20	0	8.9
Myrcene	6.2	73	0.84	0.16	0.26	0.24	2.35	0.70	0.76	16.9
d-Limonene	6.7	91	0.9	0.35	0.46	0.49	0.23	0.24	0	4.1
Terpinolene	6.2	95	1.2	0.31	0.49	0 69	0.35	0.28	0	4.9

[a] Initial HC concentration = 8 ppm compound; products in ppm compound.

Saunders et al. (59), in analyzing rainwater in the Washington, DC area, found a compound identified as 3-methyl-furan. They proposed that the furan is a by-product from the terpene photooxidation, suggesting an unusual ring closure mechanism to explain their results. However, since 3-methyl-furan has not been observed by other investigators irradiating terpenes, its production from terpene photooxidation is highly unlikely. Also, since most polluted atmospheres contain high ozone levels, the stability of this compound is very doubtful, since it oxidizes when exposed to oxygen.

The composition of aerosol particles produced from the photooxidation of terpenes with NO_x and reactions with ozone was investigated by Schuetzle and Rasmussen (60). For example, the reaction of limonene with NO_x in the presence of ultraviolet light produced over 30 aerosol products. These include aldehydes, alcohols, acids, peroxides, nitro esters of alcohols, acids and peroxides. The mass spectroscopic analyses also suggested that dimetric and possible trimeric reaction products were produced upon photooxidation. The formation of aerosols from the reaction of limonene with ozone was found to be much faster than from the photooxidation reaction. Similar products were observed with ozonolysis reactions, except for the nitrogen-containing species. The aerosols were collected on stainless steel impactor plates that collect particles greater than 0.5 μm. The collection of a smaller fraction size would have been more useful, since a considerable portion of the aerosols should be below 0.5 μm. The nephelometer used in the study suggested that the aerosols account for greater than 50% of the reacted carbon, a conclusion that qualitatively agrees with the earlier findings of Arnts and Gay. However, the nephelometer could also be missing a large amount of material because aerosols greater than 0.1 μm are not easily detected (i.e., the amount detected is not proportional to the mass).

Cronn et al. (61) surveyed particulate samples collected in southern California. Compounds that were tentatively identified by high resolution MS include pinonic acid ($C_{10}H_{16}O_3^+$), norpinonic acid ($C_8H_{12}O_4^+$), a $C_{10}H_{14}O_3$ isomer and a $C_9H_{14}O_2$ isomer. The total contribution of the peaks was only 1 $\mu g/m^3$ in the midafternoon sample (1200-1420 PST). The total mass loading during this time period for particles of $d \leq 3.5$ μm was 204 $\mu g/m^3$. The

sum of these tentatively-identified natural organic aerosols was lowest at nighttime and the evening hours. The above data suggest that the natural HC contribution to aerosol formation in the Los Angeles area is negligible.

A recent study by Hull (62) has shown pinonaldehyde, nopinone, and myrtenol as products produced from the ozonolysis of α-pinene. This study did not specify whether the products were in the gas or solid phase, since all the material collected was introduced into GC-MS.

Zimmerman et al. (63) have suggested that the oxidation of terpenoids is an important source of CO in the atmosphere. These investigators calculated that between 4.2-13.3 x 10^{14} g/yr of CO can be generated from the atmospheric photooxidation of isoprene and the terpenes. Their calculation assumes that 60-80% of the carbon in natural HC's can lead to CO formation.

The hypothesis of Zimmerman et al. has been tested recently in an EPA study with α-pinene (see Figures 8 and 9). Starting with 11.5 ppmC of α-pinene, 1.3 ppm CO was found after a 6-hr irradiation period, which corresponds to 11.5% of the original carbon. The figures show that the photooxidation of α-pinene produces high levels of aerosols, but does not produce high concentrations of CO. The aerosols are also apparently lost to the walls of the chamber, since the number, volume, and surface area of particles all decrease after 100 min of irradiation, even though all of the α-pinene does not react.

Aerosols were collected at the end of the irradiation, usually after 6 hr. The total concentration of the material found on the filter was only 1.9% of the original starting compound (with 71 mg of α-pinene in the chamber initially, and 1.3 mg of aerosol collected). Obviously, a problem exists with these experiments in terms of carbon balance, since the material was not observed in either the gas or aerosol phase. We have seen earlier from the work of Schuetzle and Rasmussen that over 50% of the organic material was observed in the aerosol phase at least for limonene and terpinolene. The aerosol data shown in Figure 9, when reasonable estimates are made with the aerosol density and aerosol composition, agree very well with the amount of material collected. These data suggest that a large fraction of organic

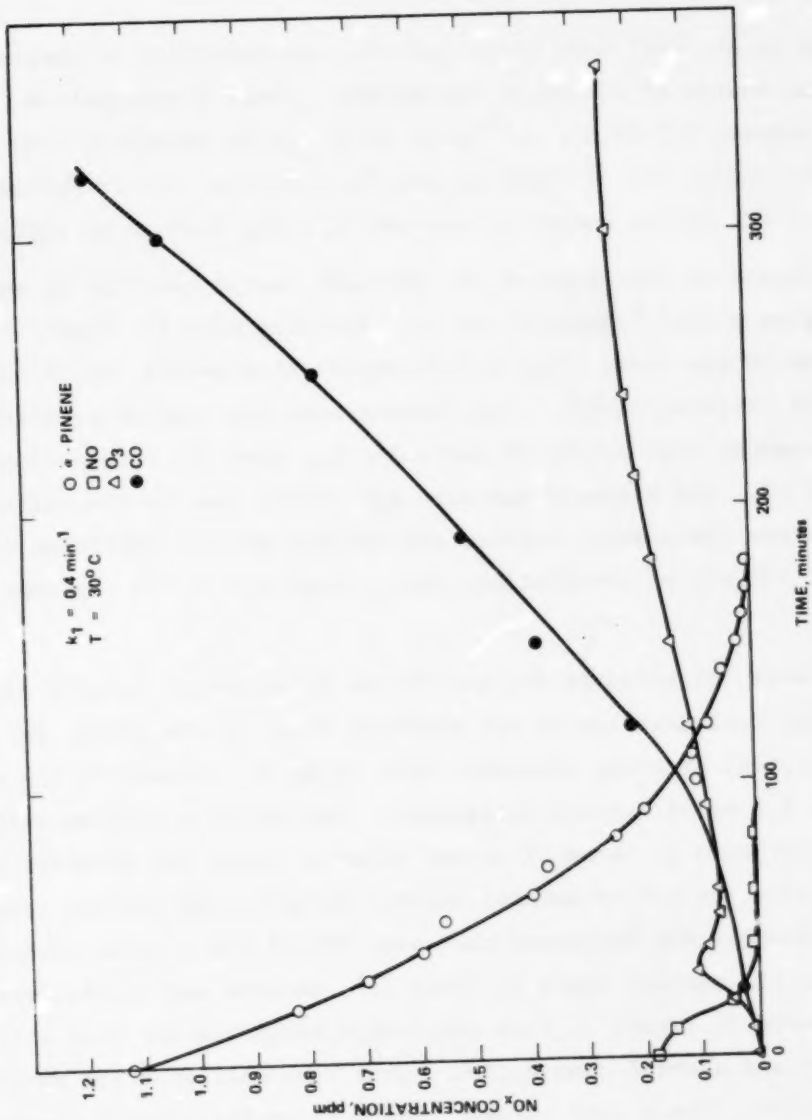

Figure 8. Data on photooxidation of alpha-pinene in the presence of NO_x.

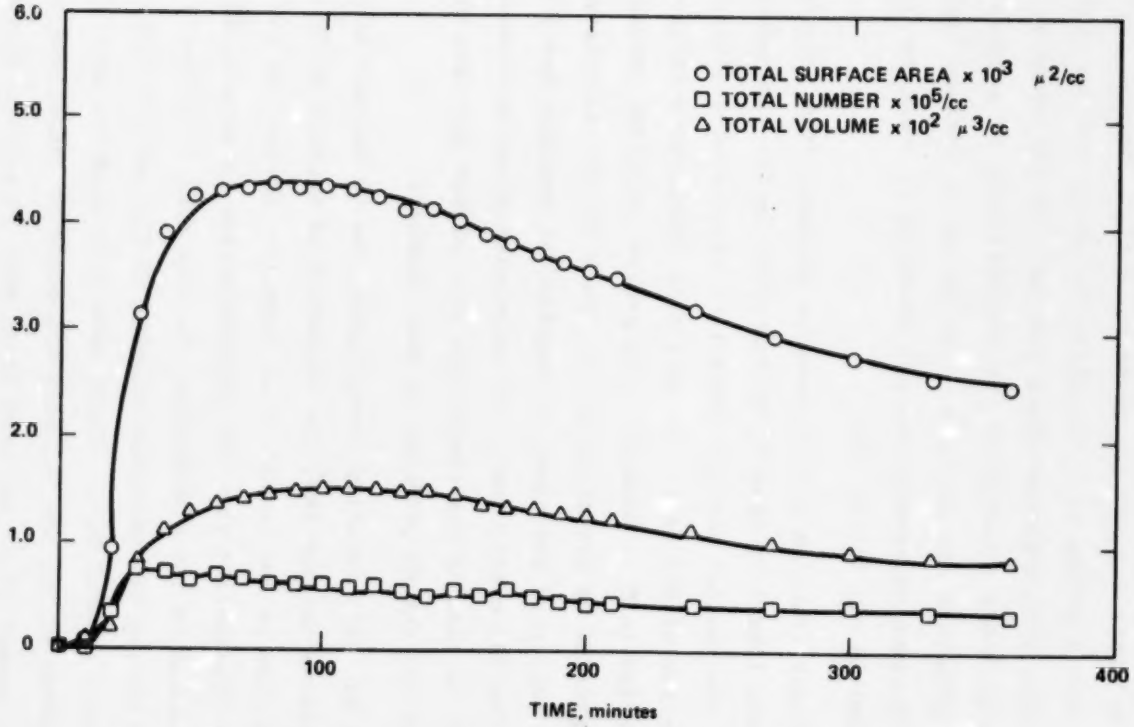

Figure 9. Aerosol data for the photooxidation of alpha-pinene.

carbon exists in the gas phase that is not measured, or that the walls of the chamber are acting as a significant sink for both aerosols and gaseous products. In light of the few gaseous products identified by FTS-IR techniques employed by Arnts and Gay (34) (see Table 8), the latter explanation appears most plausible.

The CO produced in this latest EPA study is clearly greater than that found earlier by Arnts and Gay (11.5% versus 0.6%). However, the EPA study was conducted over a period of 6 hr, while the Arnts and Gay work was conducted for 60 min, with α-pinene still remaining in the chamber. The increased yield in CO is probably a result of further oxidation of gaseous products, and the total aldehydes are also low. The EPA study further strengthens the position that gaseous oxygenates are not produced in great quantities as suggested by Ludlam and Bailey (30).

A significant fraction of the aerosols produced from terpene photooxidation is not likely to lead to CO formation in the atmosphere -- certainly not 60-80% of the reacted carbon! Duce (64) calculated a fine-particle aerosol ($d < 1\mu m$) lifetime of 4-7 days. In this time frame, more terpenoid aerosols could be converted to CO. However, this process requires several days, not the 2-5 hr suggested by Zimmerman et al. Duce further calculates that only 60-140 metric ton/yr of terpenoid is required to explain that POC in the atmosphere. The 900 metric ton/yr of terpenoids given by Zimmerman and coworkers (63) is clearly not compatible with either particle organic carbon (POC) observed nor the CO produced in smog chambers.

Harst et al. (65) recently investigated the CO balance in the atmosphere. Their calculations suggest that the oxidation of methane by OH cannot possibly give rise to the levels of CO currently present in the atmosphere. Instead, they hypothesize that the photooxidation of natural HC's accounts for the CO present in the atmosphere. To this end, experiments were performed for measuring the photodissociation of Cl_2 and subsequent reaction of Cl atoms with natural HC's. Their data with isoprene show that, with 73% of the carbon as CO_2 and CO, only 45% could be identified as CO. With α-pinene, the amount of CO was even less, with CO and CO_2 accounting for only 30% of the carbon. Only 12% of this reacted carbon could be established as CO.

Although Hanst et al. did show more CO was produced than in either the EPA study (Figure 8) or the Arnts and Gay work, the amount of CO was still low, at least for the case of α-pinene. The experimental data shown by Hanst et al. do not substantiate their conclusions, i.e., that the terpenoids are responsible for much of the CO in the atmosphere. Furthermore, these investigators have employed Cl, a fast-reacting free radical. In the atmosphere, OH radicals and O_3 are the reactive species. Possibly, the high concentration of Cl atoms could have reacted with the aerosols produced and resulted in more CO than is produced under normal atmospheric conditions. Certainly, the data shown in Figure 8 do not substantiate the Hanst hypothesis.

Interestingly, the ozone curve in the irradiation of α-pinene shown in Figure 8 first increases rapidly, later decreases, and then slowly increases throughout the irradiation. A similar observation was made by Arnts and Gay (34) with d-limonene at high HC/NO_x ratios (greater than 40/1). Arnts and Gay explained this double peak in terms of the very rapid reaction between ozone and the d-limonene, with subsequent photooxidation of the carbonyl products and NO_x later producing more ozone. This explanation is plausible for modeling efforts, since arbitrarily raising the O_3 + propylene reaction rate by a factor of 10 can produce a double ozone peak in smog chambers. But atmospheric buildup of ozone in the late afternoon is unlikely because: (1) smog chambers are atypical since they are efficient sources of NO_x, ozone production can continue when NO_x is below the detection limits of the instrument (66), and (2) in the atmosphere, the solar intensity begins to decrease late in the afternoon. Therefore, the system will be less photochemically active late in the afternoon.

A validated mechanism for the photooxidation of terpenoids cannot be written at this time. The main difficulty lies in the proper identification of the products arising from the photooxidation. In the case of isoprene, for example, only Schuck and Doyle (2) and Arnts and Gay (34) have investigated product formation. Schuck and Doyle could account for a large fraction (approximately 90%) of the original carbon (or even more than 90%, since acrolein identified by them was probably methacrolein); however, Arnts and

Gay (34) could account for only approximately 44% of the reacted carbon. They suggest that the remaining carbon may be in the aerosol phase.

A simplified mechanism is given in the Appendix for the photooxidation of the naturally-occurring HC's. Excluded from the mechanism are the inorganic reactions, since they are fairly well understood (3).

Most of the reactions shown in the Appendix start with the breaking of carbon-carbon double bonds with ozone. Obviously, the C_{10} terpenes can also react with hydroxyl radicals, and the product distribtuion does not appear to be significantly different when isoprene is reacted with OH instead of O_3. This situation will probably be true with the monoterpenes as well. In the case of p-cymene, only hydroxyl radicals are shown to react, because as shown in Table 4, the reaction with O_3 is slow.

Nitric oxide is shown with most of the reactions, even with O_3 present. Although NO and O_3 react very quickly, a small amount of NO is always present in a photochemical system (due to NO_2 photolysis). The nitric oxide is used primarily to convert the hydroperoxyl and peroxyalkyl radical to hydroxyl and alkoxyl radicals.

Organic nitrogen-containing compounds aside from PAN, were not shown. They are obviously produced, however, since RO and RCO_3 radicals can be expected to react with NO_2. As discussed earlier, Schuetzle and Rasmussen have also reported nitrogen-containing products in aerosols when terpenes were photooxidized in the presence of NO_x.

We have mentioned that a large fraction of the terpene products is expected to be in the aerosol phase, since upon reacting with OH or O_3, the fragmented oxygenated products should have a lower vapor pressure than the parent compound (the monoterpenes have a boiling point greater than 150°C). Aerosols are produced by quick condensation of the partially-degraded terpenoids on pre-existing particles.

SECTION 7

SOURCE-RECEPTOR RELATIONSHIPS

Source-receptor relationships are extremely important when considering oxidant production from natural HC's in the atmosphere, and serious questions have been raised that the published emission rates are too high. Certainly the experimentally-available ambient data do not suggest such rates. However, even if the rates are high, an unfortunate tendency exists to assume one-to-one relationships between pollutants from various sources of emissions. For example, the experimental measurements would suggest that nitric oxide emissions from power plants will not significantly affect ozone production until the air mass containing them travels 25-30 km downwind (67, 68). The reason is a very low HC/NO_x ratio. The excess NO actually decreases the ambient levels of O_3 near power plant plumes, which is quite a different case from the nitric oxide emitted by auto exhaust in the presence of HC's.

The question then can be raised as to the effect of vegetation on a city's air quality. Figure 4 shows that the maximum ozone is generated at a HC/NO_x ratio of approximately 10-20. However, the bulk of the natural HC's is emitted in rural areas where vegetation is so plentiful, and NO_x sources so few, that the HC/NO_x ratio is expected to be much higher. These ratios have been measured by EPA and Washington State University scientists (69, 70) and have been found to be as high as 60-100 (with NO_x levels near or below the sensitivity of the measuring instruments-usually less than 1-2 ppb V/V). Also, using fingerprint HC's such as acetylene or the xylenes, the major portion of the HC burden in rural areas is determined to be from anthropogenic origins. Therefore, insufficient NO_x is available to drive the photochemical reactions necessary for significant ozone production. The little that is produced is quickly titrated with excess natural HC's, which also results in consumption of natural HC's. Evidence for such reactions is shown in Table 5, where the daylight lifetimes of some natural and manmade HC's are given. The

table also shows that isoprene and α-pinene will nonetheless be transported into urban areas from forested tracts, provided the emissions of these compounds are large.

In order to assess the importance of emissions from forested areas into a city, a series of calculations was performed using a dispersion equation (71). This equation was derived from the numerical integration of infinite line sources with respect to upwind distance increments. Its general form is:

$$X = \frac{qa}{u} \int_{0}^{\text{dist.}} \frac{Xu}{q}\, dx$$

where

X = concentration of pollutant
q = source flux
u = wind speed

The calculations were made with the following boundary conditions:

(1) Meteorological stability Class 4
(2) Receptor height 2 m
(3) Emission height 10 m
(4) Inversion height 100 m
(5) Source flux (a) 100 $\mu g/m^2 min$
(6) Wind speed (U) 5 m/sec
(7) Source area 10^4 km^2
(8) Source receptor 1 km downwind.

The concentration of natural HC's found at a downwind receptor, i.e., a city 1 km downwind from a forest of 10^4 km^2, was determined to be 184 ppbC. But this concentration is unrealistically high, since (1) the emission levels assumed were very high, (2) the area assumed (10^4 km^2 of forest) was very large, and (3) the natural HC, probably isoprene within a decidous forest,

or α-pinene within a coniferous forest, is a reactive olefin that will undergo reactions with OH radicals and ozone. However, of note is that when an air quality simulation model similar to the Empirical Kinetic Modeling Approach (EKMA) (72) is employed, the 184 ppbC cannot exceed the present air quality standard of 0.12 ppm. In fact, when one considers that terpenes are not very efficient ozone producers (in terms of ozone produced per parts per million carbon), the amount produced from the 184 ppbC is less than that predicted by the air quality model which is based on propylene/n-butane mixtures.

If the above calculation is repeated with α-pinene as the natural HC, and 0.05 ppm (73) and 3×10^{-8} ppm as the steady-state concentrations of O_3 and OH, respectively, are assumed then the gas phase α-pinene observed in a city will be 81.4 ppbC. The aerosol loading would contain 102.6 ppbC (60.4 $\mu g/m^3$), assuming all the α-pinene reacts to produce aerosols.

Total particulate carbon at a concentration of 60.4 $\mu g/m^3$ is much too high. As stated earlier, a recent study (58) in the Smoky Mountains has shown that the total carbon concentration was 3.3 $\mu g/m^3$ in the fine-particulate fraction. The total carbon in both the large and small fractions was only 4 $\mu g/m^3$. Even if one assumes that all of the carbon in the area was of natural sources, the model overpredicts the aerosol burden by a factor of 15. In fact, part-if not most-of the organic aerosols were probably of anthropogenic origin, since the TNHC in the area averaged 120 ppbC, with 95% being anthropogenically produced.

The size of the source area in the above calculations is too large, because few if any areas have 10^4 km^2 of dense forest, and the largest contribution (50%) of the α-Pinene is received from the last 5 km of forests. Hence, even though a very large area was assumed, the bulk of the HC load arises from sources near the receptor.

A box-type photochemical model was also employed in order to determine the amount of ozone produced from slow emissions, HC's and NO_x. The conditions employed for this modeling effort were:

(1) Source area of 10^4 km^2

(2) Diurnal insolation (k_1 max = 0.52 min^{-1})

(3) HC emission rate at 60 $\mu g/m^2$ min; NO_x at 5 $\mu g/m^2$min

(4) Propylene as surrogate terpene

(5) O_3 initally of 40 ppb V/V

(6) 5% dilution per hour containing 40 ppb of O_3

(7) Mixing height of 1.8 km (the summer condition for NC (76)).

Propylene was chosen as the surrogate terpene since, as stated earlier, a mechanism for the photooxidation of natural HC's cannot be written. In fact, the use of propylene and a high emission rate of 60 $\mu g/m^{-2}min^{-1}$ is grossly overestimating the photochemical potential of terpenes because propylene has been shown to produce more ozone on a parts-per-million-carbon equivalent than most terpenes (Figure 4).

The Dodge (72) photochemical model used in the calculation indicates that after an irradiation period of 10 hr, the total ozone in the box of 100 x 100 x 1.8 km^3 was 70 ppb. The concentration of ozone remaining after 10 hr is actually only 30 ppb above that contained in the dilution air, suggesting that the olefin/NO_x mixture contributed very little to ozone formation. When the above calculations were repeated with no initial ozone present, and a HC/NO_x ratio of 200 (by reducing NO_x) the amount of O_3 produced after 10 hr was 12 ppb. This later ratio is more comparable to actual rural HC/NO_x conditions. One must therefore conclude that even high emission levels of 60 $\mu g/m^2$ min will not produce significant ozone concentrations.

Natural HC's emitted within urban areas could contribute to ozone formation if their emission rates were high. The HC/NO_x ratio found in many cities is favorable for O_3 production. But the amount of vegetation in urban areas is small and natural HC emissions are expected to be low. Data obtained in urban areas at a number of cities show very little isoprene and practically no C_{10} natural HC's. These data were shown in Table 6, including: Tampa, Miami, Tulsa, Houston, and Boston. As shown earlier, isoprene and α-pinene have sufficiently long lifetimes to be observed if emissions were significant either upwind from a city or within the urban center. As for the more reactive HC's their emissions must also be low, since they were not observed in any of the samples (even though the sensitivity of the measurements is 0.2 ppbC). Also, such compounds would be expected to produce copious quantities of fine-particulate aerosols, which was not observed (76). Aldehydes were also found at low concentrations (77).

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APPENDIX

REACTIONS INVOLVING SOME NATURAL HYDROCARBONS

ISOPRENE

(1) $CH_2=C(CH_3)-CH=CH_2 \xrightarrow[(NO)]{O_3} CH_2C(CH_3)CHO + H_2O + CO + CH_2O$

METHACROLEIN — FORMALDEHYDE

(2) $CH_2=C(CH_3)-CH=CH_2 \xrightarrow[(NO)]{O_3} CH_3C(O)CHCH_2 + CH_2O + H_2O + CO$

METHYLVINYLKETONE

(3) $CH_3-C(=O)-CH=CH_2 \xrightarrow[(NO)]{O_3} CH_3C(O)CHO + H_2O + CO$

METHYLGLYOXAL

(4) $CH_3-C(=O)-CH=CH_2 \xrightarrow[(NO)]{O_3} CH_3-C(=O)-C(\cdot)(H)-O\cdot + 2HO_2 + CO$

$CH_3-C(=O)-H + CO_2$

ACETALDEHYDE

(5) $CH_2=C(CH_3)-CH=CH_2 \xrightarrow[NO\ O_2]{OH} CH_2C(CH_3)CHO + CH_2O$

METHACROLEIN

(6) $CH_2=C(CH_3)-CH=CH_2 \longrightarrow HC(=O)-OH + CH_2O + HO_2 + CO$

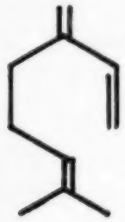
FORMIC ACID

(7) $CH_3-C(=O)-H \xrightarrow[O_2\ NO_2]{OH} CH_3-C(=O)-O-ONO_2$

PEROXYACETYLNITRATE (PAN)

MYRCENE

(8)



$\xrightarrow{O_3}$ O_3 $CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$ + $CH_2CHC(CH_2)CH_2CH_2COOH$

ACETONE — 4-METHLENE-5-HEXENOIC ACID

$CH_2CHC(CH_2)CH_2CH_2CHO$

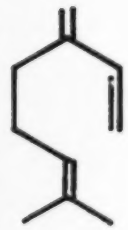
4-METHYLENE-5-HEXENAL

(9)

$\xrightarrow{O_3}$ $(CH_3)_2CCHCH_3CH_2C(O)CHCH_2$ + HCOOH

4-METHYL-4-PENTENYLVINYLKETONE

(10)

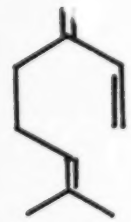


$\xrightarrow{O_3}$ $(CH_3)_2CCHCH_2CH_2C(CH_2)CHO$ + CH_2O

6-METHYL-2-METHYLENE-5-HEPTENAL

α-PINENE

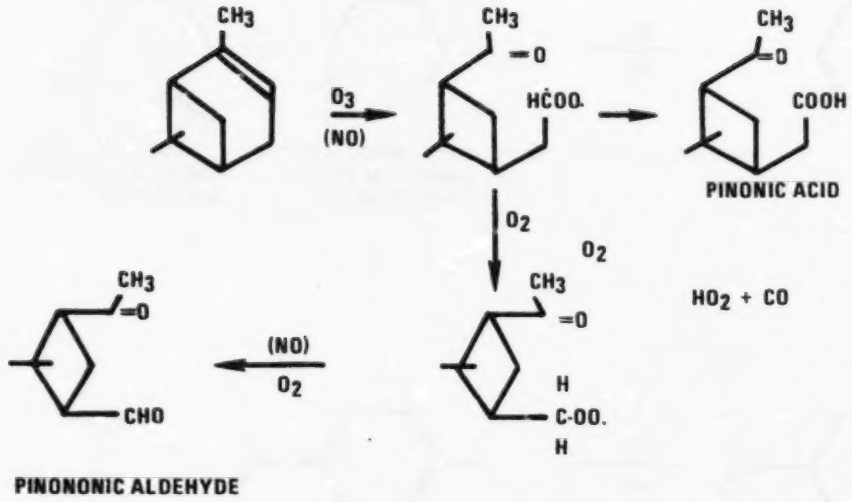
(11)



$\xrightarrow{O_3}$ $CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3$ + CH_2O + CH_2OO + $HOOCCH_2CH_2COOH$

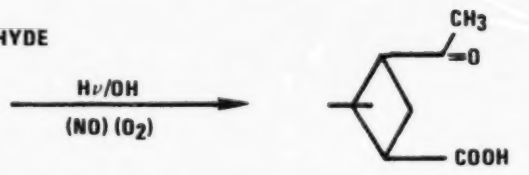
ACETONE — SUCCINIC ACID

(12)



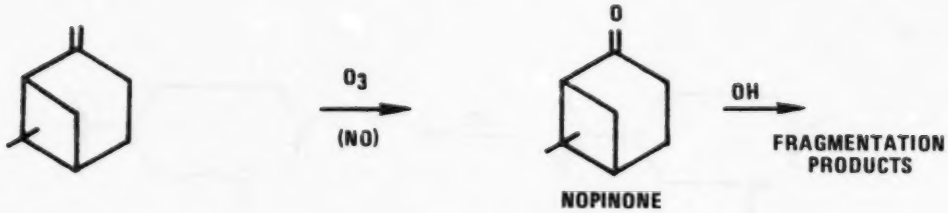
PINONONIC ALDEHYDE

PINONONIC ALDEHYDE
(13)



NORPINONIC ACID

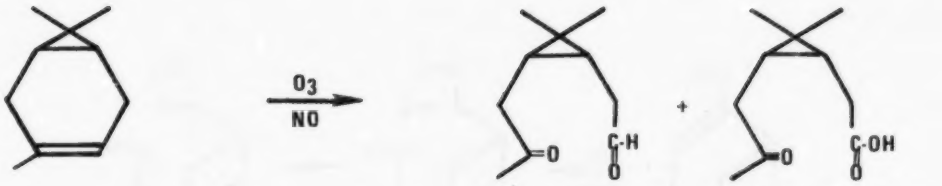
β- PINENE
(14)



NOPINONE

(15)

△- CARENE



1-ETHANAL-2, 2 DIMETHYL-3-ACETONYLCYCLOPROPANE

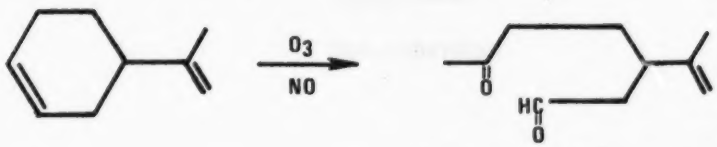
2, 2-DIMETHYL-3-ACETONYLCYCLOPROPYL ACETIC ACID

(16)

LIMONENE

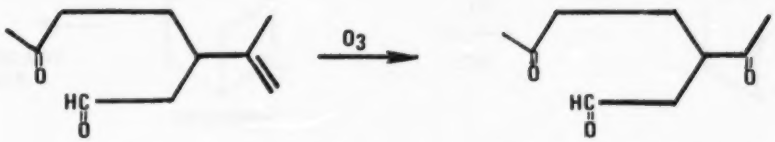
4-ACETYL-1-METHYLCYCLOHEX-1-ENE

(17)



3(2-PROPENYL)-6-KETO-HEPTANAL

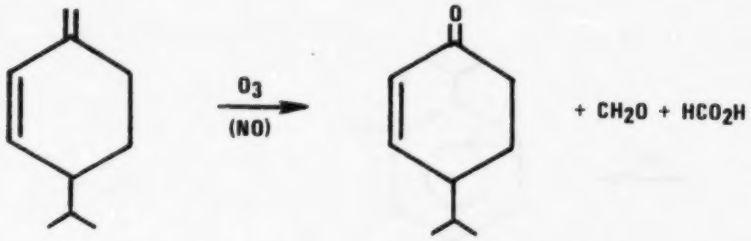
(18)



3-ACETYL-6-KETO-HEPTANAL

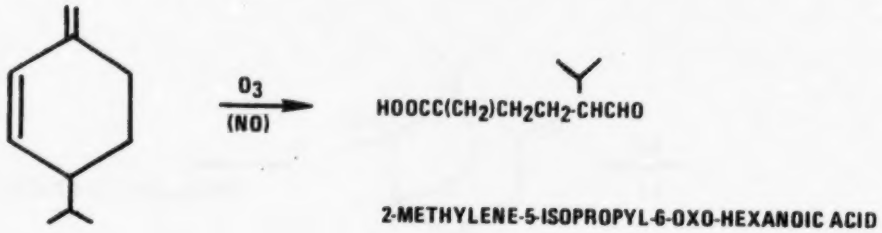
(19)

β - PHELLANDRENE



4-ISOPROPYLCYCLOHEXENONE

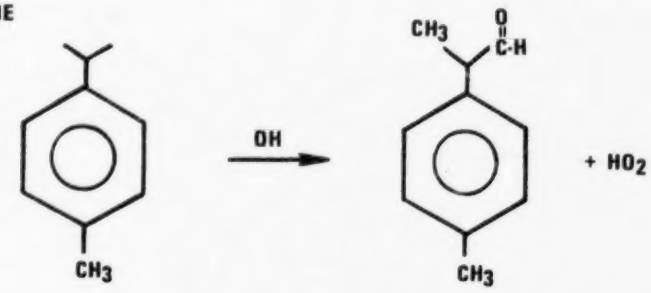
(20)



2-METHYLENE-5-ISOPROPYL-6-OXO-HEXANOIC ACID

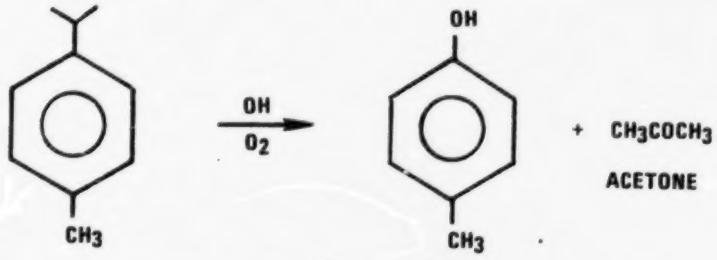
(21)

P-CYMENE



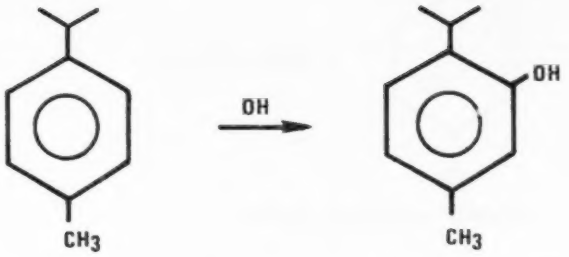
2-P-TOLYLPROPANAL

(22)



P-CRESOL

(23)



3-HYDROXY-4-ISOPROPYL TOLUENE